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THE SYNTHESIS AND THE CHARACTERIZATION OF MONOMETHYL- AND DIMETHYLINDOLES[1]

BY LÉO MARION[2] AND CATHARINE WOOLSEY OLDFIELD[2]

Abstract

All the seven monomethylindoles and 18 of the 21 possible dimethylindoles have been synthesized by unambiguous methods. Eleven were prepared by the Fischer ring closure applied to the appropriate phenylhydrazone, five of which through the appropriate phenylhydrazone of ethyl pyruvate. The rest were prepared by the Tyson ring closure. The picrates of each indole and the styphnates of all but three were prepared and their properties recorded. The three unrecorded styphnates (those of 1,6-, 5,6-, and 5,7-dimethylindole) could not be isolated without decomposition although they seemed to exist in solution.

Introduction

The degradation of alkaloids belonging to the indole group often gives rise to substituted indoles, usually monomethyl- or dimethylindoles. However, many of the dimethyl- and even of the monomethylindoles have never been reported and it is often not possible to identify such products. A case in point is the isolation among the degradation products of yohimbine (3) of a dimethylindole that has not yet been identified. Until the recent discovery by Tyson (23, 24) that potassium alcoholates are excellent agents for the formation of indoles from *o*-formotoluidides, the unambiguous synthesis of certain dimethyl- and monomethylindoles, i.e., those substituted in either the 4- or the 6-position, was not possible.

The seven monomethylindoles and 18 of the 21 dimethylindoles have now been synthesized unambiguously and their picrates and styphnates have been prepared. Each solid indole was recrystallized until the melting point was constant and, when the indole was an oil at room temperature, it was distilled twice and a middle fraction taken. Many of the indoles deteriorate on keeping unless they are sealed in evacuated tubes. However, the picrates are stable. All the picrates were recrystallized to their ultimate melting points and the styphnates at least once. The melting points of the latter are, therefore, not quite as accurate as those of the former but are sufficiently so for purposes of identification. All the recorded melting points of the picrates and styphnates were taken by immersing the substance in the bath about 20° C. below the melting point in order to avoid prolonged heating. Both the

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Contribution from the Division of Chemistry, National Research Laboratories, Ottawa, Canada. Issued as N.R.C. No. 1477.

[2] *Chemist.*

picric acid and the styphnic acid used in the preparation of these derivatives were purified by recrystallization from hot water. The properties of the indoles, their picrates, and styphnates are listed in Table I. An examination of this table reveals that any monomethyl- or dimethylindole can be identified from its properties and the melting points of its two derivatives.

TABLE I

MELTING POINTS OF MONOMETHYL- AND DIMETHYLINDOLE DERIVATIVES

Indoles, and their melting points, ° C.		Picrate, m.p., ° C.	Styphnate, m.p., ° C.
1-Methyl		151	158
2-Methyl	62	139	147
3-Methyl	96.5	182	168
4-Methyl, ††		194	170
5-Methyl	59.5	161.5	172
6-Methyl, ††		161.5	160
7-Methyl, ††	85	177.5	154
1,2-Dimethyl,††	56	125	153
1,3-Dimethyl		145	133
1,4-Dimethyl, ††		187	158
1,5-Dimethyl, †		151	144
1,6-Dimethyl, ††		148	*
1,7-Dimethyl, ††	78	154.5	150
2,3-Dimethyl	108	159	159
2,4-Dimethyl		164.5	167
2,5-Dimethyl	115	159	149
2,6-Dimethyl, ††	88.5	138.5	146
2,7-Dimethyl, ††		156.5	149
3,5-Dimethyl	75	177	184
3,7-Dimethyl	64	165	152
4,6-Dimethyl, ††		169	168.5
4,7-Dimethyl, †	102	177	173
5,6-Dimethyl, ††	64	154.5	*
5,7-Dimethyl, ††		183	*
6,7-Dimethyl, ††	70	164	162

† *Indole previously prepared but picrate not made.*

†† *Indole not previously known.*

* *These styphnates form in solution but are dissociated as soon as an attempt is made to isolate them.*

The elementary micro-analysis for nitrogen of the picrates sometimes offers difficulties but this element can then be determined by the micro-Kjehldahl method following a preliminary treatment with hydriodic acid (7).

It should be pointed out that mixed indole picrates are sometimes very difficult to separate and in such cases it is advisable to regenerate the indole, distil, and reject end fractions. Admixture of an indole picrate with another causes a depression in melting point of the order of 10° to 20° C.

The Syntheses

Although the classical Fischer indole synthesis (5) was extremely useful for the preparation of the indoles it was not always applicable, since when it is applied to *m*-substituted phenylhydrazones ring closure can take place in two different ways and give rise to a mixture of indoles. In almost all such cases, however, it was found that the method discovered by Tyson (23, 24) could be used successfully. Whenever this method was applicable it was found to be less tedious than Fischer's synthesis and generally gave better yields. The Tyson method also has its limitations and can give rise to mixtures as, for instance, when applied to 2,3,6-trimethylformanilide. The product would obviously consist of a mixture of 4,7- and 6,7-dimethylindoles. These two indoles were conveniently prepared by the Fischer synthesis.

7-Methylindole was prepared by the Fischer synthesis and although 1-, 2-, and 3-methylindoles were prepared by that method, they were also synthesized by the Tyson method (15) as well as were the remaining monomethylindoles.

With one exception all the dimethylindoles having one methyl group in position 1 were prepared from the appropriate formotoluidide by the Tyson method, which has been shown to be applicable to the formation of 1-substituted indoles (15). The Fischer synthesis was used for the preparation of 1,7-dimethylindole. It should be noted, however, that the purification of 1-substituted indoles prepared by the Tyson method was difficult because of the presence of small quantities of impurities. These impurities might, possibly, be 3-substituted homologues of the indole (21).

All the 2-substituted indoles were synthesized by the Fischer method except 2,4- and 2,6-dimethylindoles, which were obtainable readily and without ambiguity by the Tyson method. 2,3-Dimethylindole is also accessible by the latter method (15).

The dimethylindoles having substituents in positions 3,5-, 3,7-, 4,7-, and 6,7- were synthesized via the Fischer synthesis while the remaining dimethylindoles reported were obtained by Tyson's method.

Three dimethylindoles are still lacking to complete all the possible isomers. They are 3,4-, 3,6-, and 4,5-dimethylindoles. Their synthesis is under way and will be reported later.

It seemed unnecessary to give all the references relevant to this work and, therefore, only those deemed essential have been listed at the end of this paper.

Experimental

When the indole was a solid at room temperature it was recrystallized from a mixture of absolute ether and purified pentane until there was no further increase in melting point.

The picrates were prepared by adding a solution of a slight excess of the indole in ether to a solution of picric acid in ether containing a little methanol. The picrate was filtered off and recrystallized either from ether or from a mixture of ether and methanol. There was, generally, no appreciable increase of the melting points of the picrates on recrystallization.

The styphnates were prepared by the addition of a methanolic solution of styphnic acid to an ether solution of the indole. They were recrystallized once from concentrated solutions in methanol. Although some styphnates could be recrystallized from ether, this was not always possible and in some cases the ether solutions deposited styphnic acid. In such cases, the addition of a little methanol prevented the compound from dissociating, and it crystallized. There were, however, three exceptions, i.e., the styphnates of 1,6-, 5,6-, and 5,7-dimethylindoles, which it has not been possible to isolate although the colour of the solutions indicated the existence of the styphnates in solution.

The Fischer Syntheses

This synthesis involves ring closure in the appropriate phenylhydrazone by fusion with zinc chloride. With certain substituted phenylhydrazones of ethyl pyruvate better results were obtained by adding the zinc chloride to a solution of the hydrazone in α-methylnaphthalene and heating the mixture in an oil-bath. In two cases, however, it was found expedient to reflux the hydrazone with absolute ethanol and concentrated sulphuric acid, in order to bring about ring closure and indole formation.

2-Methylindole

The phenylhydrazone of acetone was obtained in 86% yield (straw-coloured oil, b.p. 139° to 142° C. (18 mm.)) from the condensation of phenylhydrazine with acetone previously distilled over potassium permanganate. It (24 gm.) was mixed with freshly fused zinc chloride (27.3 gm.) and heated over a bare flame until the vigorous exothermic reaction started. The flask was withdrawn from the flame and shaken gently until the reaction had subsided and the reaction mixture solidified. The indole was separated from the mixture by steam distillation and extraction from the distillate with ether. It consisted of an oil that crystallized on cooling. Wt. 11.0 gm., yield 53%. 2-Methylindole was distilled *in vacuo*, b.p. 140° C. (1 mm.), and the crystalline distillate recrystallized from a mixture of absolute ether and petroleum ether, m.p. 62° C.* It yielded a pure picrate without further recrystallization.

3-Methylindole

Propylidenephenylhydrazone (27 gm., b.p. 135° to 145° C. (5 mm.)), prepared in 84% yield from phenylhydrazine and propionaldehyde, was fused with zinc chloride and the 3-methylindole isolated from the mixture by steam distillation. It was distilled, b.p. 100° to 110° C. (1 mm.), and twice crystallized from petroleum ether.

2,3-Dimethylindole

The phenylhydrazone of methyl ethyl ketone (23 gm., b.p. 146° C. (16 mm.)), prepared in 71% yield, was fused with zinc chloride (27.3 gm.) and the indole

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**All melting points are corrected.*

obtained by steam-distillation of the mixture, wt. 17.6 gm., yield 85%. It was sublimed (132° to 133° C. (0.5 mm.)) and recrystallized from ether–petroleum-ether. This indole can also be prepared by the method of Tyson (15).

1,2- and 1,3-Dimethylindole

These two indoles were prepared by fusion with zinc chloride of the N-methylphenylhydrazones of acetone (b.p. 68° to 71° C. (3 mm.)) and of propionaldehyde (b.p. 101° to 105° C. (5 mm.)).

2,5- and 3,5-Dimethylindole

The necessary *p*-tolylhydrazine was prepared from purified *p*-toluidine by diazotization and reduction of the product with stannous chloride and hydrochloric acid (13). The *p*-tolylhydrazone of acetone was obtained in 82% yield, b.p. 125° to 135° C. (2 mm.), m.p. 45° to 46° C. Raschen (20) gives m.p. 50° to 52° C. The *p*-tolylhydrazone of propionaldehyde (yield 79%) boiled at 127° to 135° C. (2 mm.) . Fusion with zinc chloride of the appropriate *p*-tolylhydrazones produced respectively 2,5-dimethylindole (yield 28%, sublimes at 90° to 103° C. (0.5 mm.) m.p. 115° C.) and 3,5-dimethylindole (yield 33%, b.p. 78° to 85° C. (1 mm.), long, colourless needles, m.p. 75° C.).

2,7- and 3,7-Dimethylindole

The required *o*-tolylhydrazine was prepared according to the directions of McPherson and Stratton (13) and condensed with acetone and with propionaldehyde to obtain the corresponding *o*-tolylhydrazones. Isopropylidene *o*-tolylhydrazone (72% yield, b.p. 128° to 133° C. (4 mm.), m.p. 49° C.) fused with zinc chloride gave rise to 2,7-dimethylindole, a light-yellow oil, b.p. 80° to 86° C. (0.5 mm.), yield 6.1%. The picrate separated as slender red needles, m.p. 156.5° C. Calc. for $C_{16}H_{14}O_7N_4$: C, 51.34; H, 3.74%. Found: C, 51.16, 51.33; H, 3.91, 3.92%.

Propylidene *o*-tolylhydrazone (yield 97%, b.p. 122° to 132° C. (2 mm.)) when fused with zinc chloride produced 3,7-dimethylindole, b.p. 80° to 95° C. (0.5 mm.), in 25% yield.

Ethyl Pyruvate

Freshly distilled pyruvic acid (b.p. 64° to 67° C. (15 mm.), 616 gm.) was added to absolute ethanol (322 gm.) and refluxed for 16 hr. Ethyl pyruvate was isolated by fractionation of the product *in vacuo*, b.p. 51.5° to 53° C. (16.5 mm.), wt. 385 gm., yield 47%.

7-Methylindole

A mixture of *o*-tolylhydrazine (27 gm.) and ethyl pyruvate (29 gm.) was stirred while cooling under the tap. Ether and anhydrous sodium sulphate were added, and the solution filtered and diluted with petroleum ether. The crystalline *o*-tolylhydrazone that separated was filtered and recrystallized from 50% ethanol and from petroleum ether; colourless needles, melting at 76° to 77° C., wt. 38 gm., yield 78%. Calc. for $C_{12}H_{16}O_2N_2$: C, 65.45; H, 7.27; N, 12.73%. Found: C, 65.55, 65.25; H, 7.28, 7.40; N, 12.76%.

The ether–petroleum-ether mother-liquor, on concentration, yielded a further crop of crystals which, recrystallized from ether–petroleum-ether and from aqueous ethanol, was obtained as yellow needles melting at 62° C. In admixture with the hydrazone melting at 77° C., it melted at 50° to 55° C. Found: C, 65.83, 65.40; H, 7.47, 7.50; N, 12.86%. This second compound seems to be isomeric with, but different from, the higher melting hydrazone.

o-Tolylhydrazone of ethyl pyruvate (m.p. 77° C., in batches of about 10 gm.) was heated with fused zinc chloride at 220° C. in an oil-bath. The combined product of the reaction was warmed with dilute hydrochloric acid and, after cooling, extracted with ether. The combined ether extract was washed with dilute sodium hydroxide solution, with water, dried over anhydrous potassium carbonate, and distilled to dryness. The residual ethyl 7-methylindole-2-carboxylate was distilled *in vacuo* and the distillate which crystallized on cooling was recrystallized once from ether–petroleum-ether and twice from methanol, from which it separated as short, colourless needles melting at 131° C. Calc. for $C_{12}H_{13}O_2N$: C, 70.94; H, 6.40%. Found: C, 70.31, 70.28; H, 6.42, 6.69%. The sodium hydroxide washings from the ether solution, when acidified with hydrochloric acid, yielded a small quantity of 7-methylindole-2-carboxylic acid.

The ester, when saponified with alcoholic potassium hydroxide, yielded the corresponding acid which, twice recrystallized from water, consisted of small, colourless flat needles melting at 176° C. Calc. for $C_{10}H_9O_2N$: C, 68.57; H, 5.14%. Found: C, 68.43, 68.80; H, 5.28, 5.07%.

7-Methylindole-2-carboxylic acid (2 gm.) was decarboxylated by refluxing in the presence of quinoline (2 gm.) and a trace of copper-bronze for one hour in a metal-bath at 250° to 260° C. The mixture was cooled, dissolved in ether, and the filtered ether solution washed repeatedly with 5% hydrochloric acid, with 5% sodium carbonate solution, and with water. It was dried over anhydrous potassium carbonate, the ether distilled off and the residue distilled *in vacuo*. There was obtained 0.9 gm. of 7-methylindole (yield 60%) which, recrystallized from ether–petroleum-ether, formed glistening plates melting at 85° C. Calc. for C_9H_9N : C, 82.44; H, 6.87%. Found: C, 82.87, 82.81; H, 7.17, 7.14%. The picrate of 7-methylindole, recrystallized from methanol containing a little petroleum ether, consisted of red needles melting at 177.5° C.

1,7-Dimethylindole

o-Toluidine was converted to N-methyl-*o*-toluidine in 75% yield by the action of dimethyl sulphate. N-methyl-*o*-toluidine was purified by recrystallization of its acetyl derivative (m.p. 58° C.) and hydrolysis back to the base, b.p. 98.5° to 99° C. (17 mm.). Treatment of N-methyl-*o*-toluidine with sodium nitrite in hydrochloric acid (9) produced N-nitroso-methyl-*o*-toluidine (yield, 88%) which when reduced with zinc dust in acetic acid (8) gave rise to N-methyl-*o*-tolylhydrazine (yield, 35%). N-Methyl-*o*-tolylhydrazine (32 gm.) was condensed with ethyl pyruvate (30 gm.) and the product fractionated *in vacuo*. The N-methyl-*o*-tolylhydrazone produced, b.p. 140° to 141° C. (4 mm.), is a yellow oil; wt. 44 gm., yield, 80%. It was dissolved in α-methylnaphthalene and the solution heated with zinc chloride in an oil-bath at 150° C. for 30 min. The cooled mixture was washed repeatedly with ether and the combined ether solution distilled to dryness. The residual mixture of α-methylnaphthalene and crude ester was refluxed with alcoholic potassium hydroxide. To the cooled solution, water and ether were added and after thorough mixing the aqueous layer was separated. The ether solution was washed twice more with water and the combined aqueous solution acidified with hydrochloric acid. The precipitated 1,7-dimethylindole-2-carboxylic acid was extracted with ether and sublimed *in vacuo* (190° to 195° C. (1.5 mm.)). The sublimation was accompanied by some decomposition and the formation of a small quantity of 1,7-dimethylindole. The acid was recrystallized once from dilute acetic acid and twice from methanol from which it separated as short, colourless needles melting at 218.5° C. (decomp.), wt. 2.9 gm. Calc. for $C_{11}H_{11}O_2N$: C, 69.84; H, 5.82; N, 7.41%. Found: C, 70.31, 70.13; H, 6.01, 6.32; N, 7.33, 7.52%.

Decarboxylation of the acid by heating with quinoline and copper-bronze gave rise to 1,7-dimethylindole, b.p. 80° to 83° C. (1 mm.). Crystallized from ether–petroleum-ether it separated as colourless, well formed prisms melting at 78° C.; wt. 1.7 gm., yield, 76%. Calc. for $C_{10}H_{11}N$: C, 82.76; H, 7.59; N, 9.66%. Found: C, 82.61, 82.51; H, 7.76, 7.80; N, 9.86, 9.79%. It yielded a picrate which, recrystallized from methanol, melted at 154.5° C. Calc. for $C_{16}H_{14}O_7N_4$: C, 51.34; H, 3.74%. Found: C, 52.17; H, 4.13%.

4,7-Dimethylindole

p-Xylylhydrazine (10 gm.), prepared from *p*-xylidine by diazotization and subsequent reduction, was condensed with ethyl pyruvate (9 gm.) and the resulting xylylhydrazone (6) obtained as pale-yellow plates melting at 90° C., wt. 14 gm.; yield, 81%. Calc. for $C_{13}H_{18}O_2N_2$: C, 66.67; H, 7.69%. Found: C, 66.91, 67.16; H, 8.13, 8.07%.

An attempt to close the pyrrol ring by heating the xylylhydrazone dissolved in α-methylnaphthalene with zinc chloride resulted only in the partial saponification of the ester-xylylhydrazone to the xylylhydrazone of pyruvic acid. The latter was crystallized once from aqueous methanol and twice from petroleum ether from which it separated as small, colourless, prismatic needles melting at 173° C. Calc. for $C_{11}H_{14}O_2N_2$: N, 13.59%. Found: N, 13.72, 13.79%. Refluxing the acid xylylhydrazone (2.8 gm.) overnight with absolute ethanol and concentrated sulphuric acid not only caused esterification but also brought about ring closure and the formation of ethyl 4,7-dimethylindole-2-carboxylate, which sublimed at 105° to 110° C. ($<$1 mm.), and crystallized from ether–petroleum-ether as small, colourless plates melting at 142° C. Wt. 0.4 gm. Calc. for $C_{13}H_{15}O_2N$: C, 71.89; H, 6.91; N, 6.45%.

Found: C, 71.92, 71.80; H, 7.02, 6.97; N, 6.62, 6.65%. Refluxing the *p*-xylylhydrazone of ethyl pyruvate (5 gm.) with absolute ethanol (55 cc.) and concentrated sulphuric acid (5 cc.) for six hours yielded 1.08 gm. of ethyl 4,7-dimethylindole-2-carboxylate.

Ethyl 4,7-dimethylindole-2-carboxylate (1.3 gm.) on saponification yielded 4,7-dimethylindole-2-carboxylic acid (wt. 1.2 gm., yield 92.3%), which crystallized from aqueous ethanol as colourless, very small crystals, m.p. 208° C.

Decarboxylation of 4,7-dimethylindole-2-carboxylic acid by the usual method produced 4,7-dimethylindole in 94% yield. It crystallized from ether–petroleum-ether as very small, colourless crystals melting at 102° C. Plancher and Caravaggi (18) give the melting point as 101° to 102° C. but they did not prepare the picrate.

6,7-Dimethylindole

The 3-nitro-*o*-xylene necessary for this synthesis contained some 4-nitro-*o*-xylene, and a good separation was effected by a careful fractionation of the product through a Stedman column. The pure 3-nitro-*o*-xylene boiled at 72° C. (1 mm.) (347 gm. was obtained from 450 gm. of technical material).

3-Nitro-*o*-xylene was converted to 3-*o*-xylylhydrazine by a series of reactions parallel to those used for the synthesis of *p*-xylylhydrazine outlined above. 3-*o*-Xylylhydrazine (64 gm., m.p. 111° to 112° C.) was condensed with ethyl pyruvate (68 gm.) and the resulting 3-*o*-xylylhydrazone of ethyl pyruvate (77 gm., yield 70%) crystallized twice from petroleum ether and once from aqueous methanol, from which it separated as white needles with a slight yellowish cast, m.p. 75.5° C. Calc. for $C_{13}H_{18}O_2N_2$: N, 11.97%. Found: N, 11.98%. An attempt to effect ring closure by heating in α-methylnaphthalene solution with zinc chloride was unsuccessful and resulted in the partial hydrolysis of the ester-xylylhydrazone to the corresponding 3-*o*-xylylhydrazone of pyruvic acid, which was crystallized from acetic acid and from methanol from which it separated as fine yellow needles, m.p. 194° C. Calc. for $C_{11}H_{14}O_2N_2$: C, 64.08; H, 6.80%. Found: C, 63.92, 64.00; H, 6.95, 7.02%.

3-*o*-Xylylhydrazone of pyruvic acid (5 gm.) was refluxed for five hours with absolute ethanol (50 cc.) and concentrated sulphuric acid (5 cc.). The contents of the flask was poured into water and the gummy precipitate separated by ether extraction and distilled *in vacuo*. The ethyl 6,7-dimethylindole-2-carboxylate thus obtained (wt. 1.4 gm.), after crystallization once from ether–petroleum-ether and twice from methanol, consisted of colourless needles, m.p. 163° C. Calc. for $C_{13}H_{15}O_2N$: C, 71.89; H, 6.91; N, 6.45%. Found: C, 71.78, 71.89; H, 6.99, 7.00; N, 6.49, 6.50%. The use of larger quantities of 3-*o*-xylylhydrazone of pyruvic acid in the ring closure reaction reduced the yield considerably.

Saponification of ethyl 6,7-dimethylindole-2-carboxylate yielded the corresponding acid, which crystallized from aqueous methanol as colourless microscopic crystals, m.p. 216° C. Calc. for $C_{11}H_{11}O_2N$: C, 69.84; H, 5.82%. Found: C, 70.63, 70.40; H, 6.10, 6.04%. On decarboxylation the foregoing acid yielded 6,7-dimethylindole (79% yield) which, crystallized from ether–petroleum-ether, consisted of colourless plates, m.p. 70° C. Calc. for $C_{10}H_{11}N$: C, 82.75; H, 7.59%. Found: C, 83.59, 83.66; H, 7.65, 7.54%. 6,7-Dimethylindole picrate crystallized from methanol as dull red needles, m.p. 164° C.

1-Methylindole

Condensation of N-methylphenylhydrazine (24.4 gm.) with ethyl pyruvate (23.2 gm.) gave rise to the N-methylhydrazone of ethyl pyruvate (37.5 gm., yield 85%). After distillation, b.p. 139° to 149° C. (3 mm.), it consists of an orange-coloured oil. Ring closure was effected by heating the N-methylphenylhydrazone of ethyl pyruvate in α-methylnaphthalene with zinc chloride. The product when saponified with alcoholic potassium hydroxide yielded 1-methylindole-2-carboxylic acid (5.8 gm.) which after sublimation (155° to 160° C. ($<$1 mm.)), and crystallization from ethanol, melted at 214° C. Calc. for $C_{10}H_9O_2N$: C, 68.57; H, 5.14%. Found: C, 68.28; H, 4.98%. Decarboxylation of the acid in quinoline in the presence of copper-bronze produced 1-methylindole, 4.23 gm., yield, 97%, which boiled at 70° to 75° C. (2 mm.). 1-Methylindole has also been prepared by a different method (15).

The Syntheses by the Tyson Method

The method of indole ring closure developed by Tyson (23, 24) consists in heating the appropriate formyltoluidide with a potassium alcoholate. It has been shown by Marion and Ashford (15) to be applicable to formyltoluidides methylated on the nitrogen for the production of 1-methylindoles, to acetyltoluidides for the formation of 2-methylindoles, and to formylanilides carrying an ethyl group in the 2-position for the production of 3-methylindoles. The reaction works equally well whether potassium ethylate or potassium *tert*-butylate is used.

4-Methylindole

3-Nitro-*o*-xylene was reduced with iron powder and acetic acid (4) to the corresponding xylidine. 3-*o*-Xylidine (30 gm.) was added to 97% formic acid (12 cc.) and the mixture heated on the steam-bath overnight. After cooling, the product was dissolved in benzene and the solution washed with water, dried over anhydrous sodium sulphate, and concentrated to a small volume. Addition of petroleum ether to incipient turbidity caused the crystallization of 3-formamino-*o*-xylene which, after recrystallization from a mixture of benzene and petroleum ether, consisted of short colourless needles, m.p. 105° C., wt. 25.2 gm. Calc. for $C_9H_{11}ON$: C, 72.47; H, 7.38; N, 9.39%. Found: C, 72.65, 72.49; H, 7.42, 7.23; N, 9.34, 9.38%.

The formyl derivative (25.2 gm.) when heated with potassium (9.8 gm.) dissolved in absolute ethanol (110 cc.) according to the directions of Tyson (24) was converted to 4-methylindole, a yellowish oil, b.p. 90° C. ($<$1 mm.), wt. 3.75 gm. Even at −60° C., 4-methylindole did not crystallize. The picrate separated from methanol–ether as bright red needles, m.p. 194° C. Calc. for $C_{15}H_{12}O_7N_4$: N, 15.55%. Found: N, 15.51%.

2,4-Dimethylindole

Treatment of 3-*o*-xylidine (12 gm.) with acetic anhydride in benzene solution produced 3-acetamino-*o*-xylene (13 gm., yield 80%), which crystallized from benzene–petroleum-ether as colourless needles, m.p. 135.5° C. Yokoyama (25) reports a melting point of 133° C. 3-Acetamino-*o*-xylene, by heating with potassium *tert*-butylate, was converted to 2,4-dimethylindole, a pale-yellow oil, b.p. 94° to 96° C. (<1 mm.) (yield 56%). The picrate crystallized from ether–petroleum-ether as bronze-red needles, m.p. 164.5° C. Calc. for $C_{16}H_{14}O_7N_4$: C, 51.34; H, 3.74%. Found: C, 51.25, 51.54; H, 3.90, 3.89%.

1,4-Dimethylindole

3-Formylamino-*o*-xylene (36 gm.) was refluxed with alcoholic potassium hydroxide and methyl iodide as described by Bamberger and Wulz (2), and the 3-formylmethylamino-*o*-xylene (18 gm., yield 46%) produced was distilled *in vacuo.* It consists of a colourless oil, b.p. 97° to 99° C. (2 mm.). Calc. for $C_{10}H_{13}ON$: C, 73.62; H, 7.98; N, 8.59%. Found: C, 73.47, 73.62; H, 8.10, 8.06; N, 8.69, 8.69%. 3-Formylmethylamino-*o*-xylene when heated with potassium ethylate gave rise to 1,4-dimethylindole, a pale-yellow oil, b.p. 73° to 75° C. (0.2 mm.). The picrate separated from ether–petroleum-ether as orange-coloured needles, m.p. 187° C. Calc. for $C_{16}H_{14}O_7N_4$: C, 51.34; H, 3.74%. Found: C, 50.87, 51.04; H, 3.64, 3.67%.

6-Methylindole

p-Xylidine (2,5-dimethylaniline) was purified by the methods of Hodgkinson and Limpach (10) and of Morgan and Hickinbottom (17) and then fractionated *in vacuo.* The fraction boiling at 73° to 74° C. (2 mm.) was used. *p*-Xylidine by treatment with 87% formic acid, as already described, was converted to formamino-*p*-xylene, which crystallized from benzene–petroleum-ether as soft colourless needles, m.p. 119° C. Calc. for $C_9H_{11}ON$: N, 9.39%. Found: N, 9.35%.

Heating formamino-*p*-xylene with potassium *tert*-butylate produced 6-methylindole in 36% yield. The indole is a pale-yellow oil, b.p. 75° to 78° C. (1 mm.), which yields a picrate crystallizing from ether–petroleum-ether as orange-coloured needles, m.p. 161.5° C. Calc. for $C_{15}H_{12}O_7N_4$: C, 50.00; H, 3.33%. Found: C, 50.00, 50.17; H, 3.13, 3.43%.

2,6-Dimethylindole

Acetamino-*p*-xylene was prepared in 83% yield from *p*-xylidine (2,5-dimethylaniline) and acetic anhydride. It separates from aqueous methanol as long, colourless needles, m.p. 142° C. It (22.5 gm.) was converted, by heating with potassium *tert*-butylate, to 2,6-dimethylindole (10 gm., yield 50%), which crystallizes from ether–petroleum-ether as long, colourless needles, m.p. 88.5° C. Calc. for $C_{10}H_{11}N$: N, 9.65%. Found: N, 9.52.

9.67%. The picrate is obtained by crystallization from ether–petroleum-ether as brick-red needles, m.p. 138.5° C. Calc. for $C_{16}H_{14}O_7N_4$: C, 51.34; H, 3.74%. Found: C, 51.39, 51.49; H, 3.88, 3.76%.

1-6-Dimethylindole

Formylmethylamino-*p*-xylene, prepared by refluxing formylamino-*p*-xylene with alcoholic potassium hydroxide and methyl iodide (2) is a colourless oil, b.p. 99° to 100.5° C. (3 mm.). Yield, 51%. Calc. for $C_{10}H_{13}ON$: C, 73.62; H, 7.98; N, 8.59%. Found: C, 73.82, 73.61; H, 8.12, 7.90; N, 8.77, 8.78%. With the aid of potassium *tert*-butylate it was converted to 1,6-dimethylindole, which is a yellow oil, b.p. 68° to 73° C. (0.2 mm.). The picrate crystallizes from absolute ether as dark red needles, m.p. 148° C. Calc. for $C_{16}H_{14}O_7N_4$: N, 14.97%. Found: N, 14.91%.

5-Methylindole

2,4-Dimethylaniline was prepared by the nitration of *m*-xylene and reduction of the 2,4-dimethylnitrobenzene with tin and hydrochloric acid. The resulting 2,4-dimethylaniline was purified through its acetate (14, 15) and distilled, b.p. 76.5° to 78° C. (3 mm.). It was converted by the usual method to 2,4-dimethylformanilide, which crystallizes from benzene as large colourless prisms, m.p. 115° to 116° C. Calc. for $C_9H_{11}ON$: N, 9.39%. Found: N, 9.38, 9.47%. 2,4-Dimethylformanilide, with the aid of potassium alcoholate, gives rise to 5-methylindole (yield 27%), which crystallizes from ether–petroleum-ether as glistening prismatic needles, m.p. 59.5° C. The picrate was obtained as red needles, m.p. 161.5°C. Calc. for $C_{15}H_{12}O_7N_4$: N, 15.55%. Found: 15.53, 15.58%.

1,5-Dimethylindole

4-Formylmethylamino-*m*-xylene was obtained by refluxing a mixture of 2,4-dimethylformanilide with alcoholic potassium hydroxide and methyl iodide (2). It is a colourless oil with a slight yellowish cast, b.p. 99° to 100° C. (2 mm.). Yield, 29%. Calc. for $C_{10}H_{13}ON$: C, 73.62; H, 7.98; N, 8.59%. Found: C, 73.55, 73.61; H, 8.07, 8.09; N, 8.72, 8.79%. Heating 4-formylmethylamino-*m*-xylene (21.5 gm.) with potassium ethylate produced a very low yield of 1,5-dimethylindole (0.32 gm.), which is a light yellow oil, b.p. 60° to 65° C. (1 mm.). The picrate separated from ether–petroleum-ether as red needles, m.p. 151° C. Calc. for $C_{16}H_{14}O_7N_4$: C, 51.34; H, 3.74%. Found: C, 51.12; H, 3.95%.

2,3,5-Trimethylaniline

The pseudocumidine (2,4,5-trimethylaniline) necessary as a starting material was obtained by the careful fractionation of commercial 'cumidine' through a Stedman column. The fraction boiling at 106° to 110° C. (11 mm.) crystallized when cooled in dry-ice and acetone. The crystals were filtered through a cooled fritted glass funnel and the filtrate was refractionated. A further fraction, b.p. 106° to 110° C. (11 mm.), thus obtained yielded a second crop of crystals of 2,4,5-trimethylaniline. The combined crystalline material, recrystallized from petroleum ether, melted at 66° C. It was converted (yield, 84%) to 2,4,5-trimethylacetanilide, which crystallized from dilute acetic acid as fine, colourless needles, m.p. 164° C. (11) and this, when nitrated at 0° C. with concentrated nitric acid produced 6-nitro-2,4,5-trimethylacetanilide (12), which, after crystallization from ethanol, melted at 199° C., yield 82%. Hydrolysis of this nitro product with concentrated sulphuric acid (11) yielded 6-nitro-2,4,5-trimethylaniline (yield 63%) as bright orange-coloured crystals, m.p. 48° C. The amino group was removed by Mai's method (14) applied according to the directions of Adams and Kornblum (1). 6-Nitro-2,4,5-trimethylaniline (30.3 gm.) was heated on the steam-bath with 1 : 1 hydrochloric acid (500 cc.) and, when most had dissolved, the mixture was cooled with vigorous mechanical stirring. The mixture was diazotized at 5° to 10° C. with a solution of sodium nitrite (12.5 gm.) in water (30 cc.) added slowly in the course of 20 min. The stirring was continued for 30 min. more and the solution rapidly filtered and added to 30% hypophosphorous acid (325 cc.). The resulting solution was kept in the refrigerator for 10 hr. and then at room temperature for 11 hr. Cracked ice was added, the solution basified with sodium hydroxide, and the oil that separated was collected in ether. The ether extract was washed with water, dried over anhydrous potassium carbonate, and distilled to dryness. The residual nitropseudocumene (6-nitro-1,2,4-trimethylbenzene) was distilled *in vacuo*, b.p. 139° to 140° C. (7 mm.), wt. 17 gm., yield 61%. Reduction of the nitropseudocumene with iron powder and glacial acetic acid gave a 92% yield of the corresponding pseudocumidine (2,3,5-trimethylaniline), m.p. 39° C.

4,6-Dimethylindole

2,3,5-Trimethylaniline (15 gm.) was heated with 87% formic acid (6 cc.) and the resulting 2,3,5-trimethylformanilide (17.2 gm., yield 95%) crystallized from benzene, m.p. 135.5° C. Calc. for $C_{10}H_{13}ON$: N, 8.59%. Found: N, 8.65%. Heating 2,3,5-trimethylformanilide (17 gm.) with potassium (6 gm.) and *tert*-butyl alcohol (125 cc.) produced 4,6-dimethylindole, a yellowish oil, b.p. 90° to 95° C. (0.4 mm.), wt. 1.95 gm. The picrate separated from methanol in long dull dark-red needles, m.p. 169° C. Calc. for $C_{16}H_{14}O_7N_4$: C, 51.34; H, 3.74%. Found: C, 51.59, 51.45; H, 3.95, 4.06%.

*5,6-Dimethylindole**

Pseudocumidine melting at 66° C. (2,4,5-trimethylaniline) was converted by heating overnight with formic acid to 2,4,5-trimethylformanilide, which, after recrystallization from ethanol–ether, melted at 123.5° C. Yield, 90%. Heating 2,4,5-trimethylformanilide with potassium *tert*-butylate produced 5,6-dimethylindole, yield 17%. The indole distilled at 85° C. (0.5 mm.) and crystallized from petroleum ether as colourless needles, m.p. 64° C. The picrate crystallized as bright-red needles, m.p. 154.5° C. Calc. for $C_{16}H_{14}O_7N_4$: C, 51.34; H, 3.74%. Found: C, 52.04, 52.19; H, 4.20, 4.42%.

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* *This indole was prepared by Dr. W. R. Ashford.*

5,7-Dimethylindole

Mesitylene and nitromesitylene were prepared according to the methods outlined in Organic Syntheses (16, 19). Nitromesitylene was reduced with tin and hydrochloric acid to mesidine (yield 58%) and the latter when heated with formic acid produced a 93% yield of formomesidide, which crystallized from ethanol as glistening, colourless needles, m.p. 182° C. Formomesidide (27 gm.) heated with potassium *tert*-butylate produced 5,7-dimethylindole (5 gm., yield 18%), which is a light-yellow oil, b.p. 80° to 84° C. (< 1 mm.). The picrate crystallized from ether–petroleum-ether in dark red needles, m.p. 183° C. Calc. for $C_{16}H_{14}O_7N_4$: C, 51.34; H, 3.74%. Found: C, 51.41, 51.14; H, 3.91, 3.82%.

Acknowledgments

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SULPHANILAMIDOPYRIMIDINES[1]

By Leonard C. Leitch[2], Bruce E. Baker[3], and Leo Brickman[4]

Abstract

The syntheses of 2-sulphanilamido-4-hydroxypyrimidine, 2-sulphanilamido-4,6-dihydroxypyrimidine, and several other sulphanilamidopyrimidines are described. An improved method for the preparation of sulphaguanidine is given.

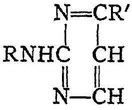
Introduction

In the course of a program of work relating to sulphanilamide derivatives, we found it necessary to synthesize 2-sulphanilamido-4-hydroxypyrimidine and 2-sulphanilamido-4,6-dihydroxypyrimidine. We found that acetylsulphanilyl chloride would not react either with 2-amino-4-hydroxypyrimidine, in agreement with the observation of Raiziss and Freifelder (10), or with 2-amino-4,6-dihydroxypyrimidine. 2-Sulphanilamido-4-hydroxypyrimidine (VI) was synthesized by the three methods outlined in Chart I.

In Scheme *A*, 2-amino-4-hydroxypyrimidine (I) was converted successively to 2-amino-4-chloropyrimidine (II) by means of phosphorus oxychloride, then to 2-amino-4-methoxypyrimidine (III) by reaction with sodium methoxide, and then to 2-acetylsulphanilamido-4-methoxypyrimidine (IV) by coupling with acetylsulphanilyl chloride. Compound (IV) was deacetylated to (V) and then demethylated to the desired 2-sulphanilamido-4-hydroxypyrimidine (VI).

Chart I

Scheme A



I $R = H, R' = OH$

II $R = H, R' = Cl$

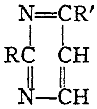
III $R = H, R' = CH_3O-$

IV $R = CH_3CONHC_6H_4SO_2-, R' = CH_3O-$

V $R = NH_2C_6H_4SO_2-, R' = CH_3O-$

VI $R = NH_2C_6H_4SO_2-, R' = OH$

Scheme B

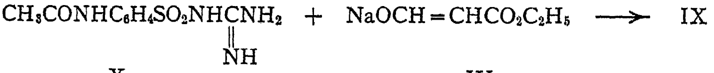


VII $R = CH_3S-, R' = OH$

VIII $R = NH_2SO_2C_6H_4NH-, R' = OH$

IX $R = CH_3CONHC_6H_4SO_2NH-, R' = OH$

Scheme C



$$\underset{\text{X}}{CH_3CONHC_6H_4SO_2NH\underset{\underset{NH}{\|}}{C}NH_2} + \underset{\text{XI}}{NaOCH{=}CHCO_2C_2H_5} \longrightarrow \text{IX}$$

X XI

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Contribution from the Research Laboratories of Monsanto (Canada) Limited, LaSalle, Que.

[2] *Formerly Research Chemist, Monsanto (Canada) Limited, La Salle, Que.; now, Chemist, National Research Laboratories, Ottawa, Canada.*

[3] *Formerly Research Chemist, Monsanto (Canada) Limited, La Salle, Que.; now Lecturer, Macdonald College, Que.*

[4] *Formerly Chief Chemist, Monsanto (Canada) Limited, La Salle, Que.; now Consulting Chemist, Brickman and Co., Montreal, Que.*

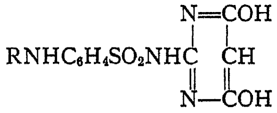
In Scheme *B*, 2-methylmercapto-4-hydroxypyrimidine (VII) was condensed with acetylsulphanilamide to give 2-acetylsulphanilamido-4-hydroxypyrimidine (IX), which was then deacetylated to (VI). If sulphanilamide was used in the condensation in place of acetylsulphanilamide, the product obtained was (VIII), substitution taking place on the amino rather than the amido group.

In Scheme *C*, acetylsulphaguanidine (X) was condensed with sodium formylacetic ester (XI) to give (IX), which was then deacetylated to the desired compound (VI). Ganapathi and co-workers (4) prepared this compound directly from sulphaguanidine and formylacetic ester.

The same three methods were applied in an attempt to synthesize 2-sulphanilamido-4,6-dihydroxypyrimidine but the results were not so gratifying. 2-Amino-4,6-dihydroxypyrimidine was substituted for (I) in Scheme *A* and was successfully carried through the first four steps of the reaction to 2-sulphanilamido-4,6-dimethoxypyrimidine, but attempts to demethylate this compound gave rise to decomposition products and none of the desired compound could be isolated.

When 2-methylmercapto-4,6-dihydroxypyrimidine was substituted for (VII) in Scheme *B*, the desired reaction did not take place and only unchanged acetylsulphanilamide was recovered from the reaction mixture.

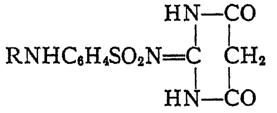
Applying Scheme *C*, it was found that acetylsulphaguanidine (X) reacted smoothly with malonic ester in the presence of sodium ethoxide to give 2-acetylsulphanilamido-4,6-dihydroxypyrimidine (XII).



$$\begin{array}{rl} & N{=}COH \\ RNHC_6H_4SO_2NHC & \quad CH \\ & N{-}COH \end{array}$$

XII R = CH_3CO-

XIII R = H



$$\begin{array}{rl} & HN{-}CO \\ RNHC_6H_4SO_2N{=}C & \quad CH_2 \\ & HN{-}CO \end{array}$$

XIV R = CH_3CO-

XV R = H

On deacetylation, 2-sulphanilamido-4,6-dihydroxypyrimidine (XIII) was obtained. This same compound could be obtained directly in excellent yields by condensing sulphaguanidine with malonic ester in the presence of sodium ethoxide. Curiously enough, (XII) and (XIII) were soluble not only in alkalies and alkali carbonates, but in alkali bicarbonates as well. Furthermore, (XII) reacted with one equivalent, and (XIII) with two equivalents, of nitrous acid. This is in agreement with the observation of Traube (13), who found that 2-amino-4,6-dihydroxypyrimidine reacted with nitrous acid to form the 5-oximino derivative. Compounds (XII) and (XIII) probably exist mainly in the oxo forms (XIV) and (XV). The active methylene group situated between the two carbonyl groups in the pyrimidine ring would account for the reactions described above.

Pharmacology

2-Sulphanilamido-4-hydroxypyrimidine and 2-sulphanilamido-4,6-dihydroxypyrimidine, as well as sulphanilylthiourea (7), were tested *in vivo* against influenza and rabic virus infections in mice. No significant cures were found. Against *Pneumococcus* (McGovern type I) in mice, these compounds were inferior to sulphadiazine, and against *Streptococcus hemolyticus* they were inferior to sulphanilamide. The two pyrimidine compounds were ineffective when administered orally to malaria-infected ducks while the thiourea showed no activity when tested against *Trypanosoma equiperdum* in rats.

Experimental

Synthesis of 2-Sulphanilamido-4-hydroxypyrimidine

Scheme A

2-Amino-4-hydroxypyrimidine was prepared according to the directions of Roblin *et al.* (11). This was converted to 2-amino-4-chloropyrimidine as described by Gabriel and Colman (3), and then to 2-amino-4-methoxypyrimidine according to Adams and Whitmore (1). This compound was coupled with acetylsulphanilyl chloride and deacetylated to 2-sulphanilamido-4-methoxypyrimidine as described by Roblin and co-workers (12). The demethylation was carried out by dissolving the material in concentrated hydrochloric acid and evaporating the solution to dryness on the steam-bath (6). The residue was taken up in water and neutralized with sodium bicarbonate solution. The product, 2-sulphanilamido-4-hydroxypyrimidine, melted at 269° to 271° C.* either alone or admixed with the material prepared by means of Schemes *B* and *C*.

Scheme B

2-Methylmercapto-4-hydroxypyrimidine was prepared by the method of Wheeler and Merriam (15). This product (3.5 gm., 0.025 mole) was added in small portions to molten acetylsulphanilamide (5.5 gm., 0.025 mole) over a period of one hour, with good stirring. The mixture was kept immersed in an oil-bath at 230° C. Evolution of methylmercaptan took place slowly. The reaction mixture was poured into water and then digested with 2% aqueous sodium hydroxide (50 ml.) until solution was complete. The solution was filtered with carbon black and neutralized with dilute acetic acid. The crude 2-acetylsulphanilamido-4-hydroxypyrimidine weighed 4 gm. A sample recrystallized from water melted at 263° to 264° C. either alone or when mixed with the 2-acetylsulphanilamido-4-hydroxypyrimidine prepared under Scheme *C*.

Deacetylation with aqueous sodium hydroxide gave 2-sulphanilamido-4-hydroxypyrimidine melting at 270° to 272° C. It was identical with the material obtained by the other two methods.

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* *Melting points are uncorrected.*

When the reaction was carried out by adding the 2-methylmercapto-4-hydroxypyrimidine to sulphanilamide in molten phenol at 175° C. (5), the product obtained was the isomeric N^4-(4-hydroxypyrimidine-2)-sulphanilamide. This product melted at 288° to 290° C. It did not give an azo colour reaction with nitrous acid and 2-naphthol and could not be titrated with standard sodium nitrite solution; this indicated the absence of a free amino group. Calc. for $C_{10}H_{10}O_3N_4S$: N, 21.0%. Found: N, 20.7%.

Scheme C

Sodium formylacetic ester was prepared by adding dropwise a mixture of ethyl acetate (44 gm., 0.5 mole) and ethyl formate (37.0 gm., 0.5 mole) to finely divided sodium (11.5 gm., 0.5 mole) in absolute ether (100 ml.). The reaction mixture was cooled by means of running water. When the sodium had completely reacted, the ether was distilled off and the residue dissolved in absolute ethanol. Acetylsulphaguanidine (40 gm., 0.15 mole) was added and the mixture stirred and refluxed for five hours. The suspended solids were filtered off, washed with a little ethanol, stirred up with warm water (500 ml.) and filtered. The insoluble material was unchanged acetylsulphaguanidine and weighed 13.0 gm. The filtrate on acidification gave 19.5 gm. (40.5%) of 2-acetylsulphanilamido-4-hydroxypyrimidine. A sample recrystallized from water melted at 263° to 264° C. Calc. for $C_{12}H_{12}O_4N_4S$: N, 18.2%. Found: N, 18.2%.

The acetyl compound (12 gm., 0.039 mole) was refluxed for 30 min. with 50 ml. of 4 *N* hydrochloric acid. The solution was filtered with carbon black and neutralized with a solution of sodium acetate. The yield of 2-sulphanilamido-4-hydroxypyrimidine was 9.0 gm. (86.5%). A sample recrystallized from water melted at 269° to 270° C., in good agreement with the melting point given by Ganapathi (4) for this compound. Calc. for $C_{10}H_{10}O_3N_4S$: total N, 21.0%; amino N, 5.26%. Found: total N, 20.9%; amino N, 5.4%.

Synthesis of 2-Sulphanilamido-4,6-dihydroxypyrimidine

Scheme A

2-Amino-4,6-dihydroxypyrimidine was prepared as described by Michael (9). This was converted to 2-amino-4,6-dichloropyrimidine according to the directions of Büttner (2) and then to 2-amino-4,6-dimethoxypyrimidine (1, 6). This was coupled with acetylsulphanilyl chloride (12) to give 2-acetylsulphanilamido-4,6-dimethoxypyrimidine, which melted at 235° to 236° C. after one recrystallization from ethanol. Calc. for $C_{14}H_{16}O_5N_4S$: N, 15.9%. Found: N, 15.7%. Deacetylation with aqueous sodium hydroxide gave 2-sulphanilamido-4,6-dimethoxypyrimidine, which after recrystallization from ethanol melted at 170° to 172° C. Calc. for $C_{12}H_{13}O_4N_4S$: N, 18.1%. Found: N, 17.9%. All attempts to demethylate this product resulted in decomposition.

Scheme B

Thiobarbituric acid was prepared by the method of Michael (8). The product was soluble in bicarbonate as well as carbonate. It was converted to 2-methylmercapto-4,6-dihydroxypyrimidine according to the directions of Wheeler and Jamieson (14). It was treated with molten acetylsulphanilamide as described under Scheme *B* above. The only product which could be isolated from the reaction mixture was unchanged acetylsulphanilamide.

Scheme C

To a solution of sodium ethoxide (from 40 gm. of sodium and 600 ml. of ethanol) was added malonic ester (80 gm., 0.5 mole) followed by acetylsulphaguanidine (90 gm., 0.35 mole). The mixture was stirred and refluxed for five hours. After cooling, the solution was filtered, the insoluble product taken up in water (600 ml.) and carefully acidified with 6 *N* hydrochloric acid. There was obtained 73 gm. (64%) of product. The 2-acetylsulphanilamido-4,6-dihydroxypyrimidine thus obtained had no definite melting point, but decomposed gradually above 162° C. It was soluble in alkalies, alkali carbonates, and bicarbonates, but insoluble in acids. It was purified by reprecipitation from sodium hydroxide solution. Calc. for $C_{12}H_{12}O_5N_4S$: N, 17.2%. Found: N, 17.3%. The product, dissolved in acetic acid, was titrated with sodium nitrite solution. One mole of the material consumed 0.96 mole of sodium nitrite.

The product (12.5 gm., 0.0385 mole) was deacetylated by heating to 95° C. with sodium hydroxide (6 gm., 0.15 mole) in water (25 ml.) for several minutes and then allowing the solution to cool slowly. After diluting and filtering with carbon black, it was acidified with dilute hydrochloric acid. The yield of 2-sulphanilamido-4,6-dihydroxypyrimidine was 10 gm. (91.7%); it melted at 248° to 249° C. Calc. for $C_{10}H_{10}O_4N_4S$: N, 19.9%. Found: N, 19.5%. On titration with standard sodium nitrite, one mole of the material consumed 2.06 equivalents of sodium nitrite.

When the reaction with malonic ester was carried out as described above but substituting sulphaguanidine for acetylsulphaguanidine, there was obtained 88.5% of 2-sulphanilamido-4,6-dihydroxypyrimidine melting at 250° to 251°C. It was identical in every respect with the material obtained by deacetylation as described above.

The sulphaguanidine used in the above experiment was prepared by the following modification of the method previously described (7). In this new method, sulphaguanidine was obtained directly in one operation from calcium acetylsulphanilylcyanamide and ammonia. The calcium acetylsulphanilylcyanamide (260 gm., 0.5 mole), prepared as described in the previous paper (7), was placed in a cast-iron steam-jacketted autoclave fitted with a high-speed agitator (600 r.p.m.) and a thermometer well. Concentrated ammonia water (200 ml.), diluted to 600 ml., was added and the mixture heated and stirred at 155° C. for four hours. At the end of this time, the reaction vessel was cooled to room temperature and the insoluble product was filtered from the reaction mixture. The crude sulphaguanidine, after drying at 110° C., weighed 105 gm. It was recrystallized from 2000 ml. of boiling water, using a small amount of carbon black to decolorize the solution. The pure sulphaguanidine, (90 gm., 42%), melted at 187° to 189° C.

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THE SYNTHESIS OF DI- AND TRITHIOLS[1]

By S. D. Simpson[2]

Abstract

In the course of a study of antidotes to lewisite the following thiols have been prepared from the corresponding di- and trihalides by the action of sodium hydrosulphide or ammonium hydrosulphide in ethanol under pressure: 1,2-dimercaptoethane, 1,2-dimercaptopropane, 1,3-dimercaptopropane, 1,2,3-trimercaptopropane, 1,2-dimercapto-*n*-butane, 2,2′-dimercaptoethyl ether, 3,3′-dimercaptopropyl ether, 2,2′-dimercaptoisopropyl ether, and 1,3-dimercapto-2-propanol.

1,2-Dimercaptopropane has been prepared by a new method, namely, by the interaction of ammonium hydrosulphide and allyl bromide. This method involves the addition of hydrogen sulphide to an unsaturated compound by the action of ammonium hydrosulphide in ethanol under pressure.

The toxicity of the above thiols and their antidotal activity to lewisite have been compared with those of 2,3-dimercaptopropanol (BAL, British anti-lewisite) and the results of these studies will be published later.

Introduction

Previous to World War II there was evidence that the toxicity of trivalent arsenical compounds is related to their reaction with essential thiol groups in the organism (12, 18). It had been shown that monothiols give some protection against the toxic action of arsenical compounds (3, 13, 19). In 1940, Peters, Stocken, and Thompson showed that 2,3-dimercaptopropanol is effective against the toxic actions of lewisite and other arsenical compounds. This dithiol subsequently became known as BAL (British anti-lewisite). A review of work on BAL has been published by Peters, Stocken, and Thompson (10). Waters and Stock (20) have described researches on BAL in the United States, and Canadian researches on BAL have been reviewed by Young (22). The thiols described herein were prepared in an attempt to find an agent that would be more suitable than 2,3-dimercaptopropanol as an antidote to lewisite, and in the hope that information would be gained concerning the relation of the structure of thiols to their toxicity and antidotal activity (14).

The synthesis of the following thiols is described below: 1,2-dimercaptoethane, 1,2-dimercaptopropane, 1,3-dimercaptopropane, 1,2,3-trimercaptopropane, 1,2-dimercapto-*n*-butane, 2,2′-dimercaptoethyl ether, 3,3′-dimercaptopropyl ether, 2,2′-dimercaptoisopropyl ether, and 1,3-dimercapto-2-propanol. The results obtained when the above-mentioned thiols and also 2,3-dimercaptopropanol were tested for their toxicity and antidotal actions have been reported (15) and will be published later. No reference has been found to the previous preparation of 1,2-dimercapto-*n*-butane, 2,2′-dimercaptoethyl ether, 3,3′-dimercaptopropyl ether, or 2,2′-dimercaptoisopropyl ether. All the thiols

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Contribution from the Department of Biochemistry, University of Toronto, Toronto, Ont.

[2] *Graduate Student.*

described herein were prepared by the interaction of organic halides and sodium hydrosulphide or ammonium hydrosulphide in ethanol under pressure.

Some of the thiols described herein have been prepared previously by the action of sodium or potassium hydrosulphide on the corresponding halide. These preparations, however, were carried out at atmospheric pressure in an open vessel (1, 2, 4-8, 11, 16, 21). Previous to the present work, investigators at Oxford had prepared several dithiols by the interaction of sodium hydrosulphide or ammonium hydrosulphide and the appropriate halide under pressure (10).

One dithiol, 1,2-dimercaptopropane, was prepared by the action of ammonium hydrosulphide on allyl bromide.

$$CH_2 : CH \,.\, CH_2Br + 2NH_4SH \longrightarrow CH_3 \,.\, CH(SH) \,.\, CH_2SH + NH_3 + NH_4Br.$$

The identity of the compound obtained in this reaction was established by analysis and by comparison of its properties with those of 1,2-dimercaptopropane and 1,3-dimercaptopropane prepared from the corresponding dihalogen compounds. The above type of reaction is of interest as it would appear to be applicable to the synthesis of other thiols.

Reagents and Methods

The thiols were synthesized by the methods described below. An organic halide was allowed to react with either sodium hydrosulphide or ammonium hydrosulphide in ethanol. Two molecules of ammonium or sodium hydrosulphide were used for each halogen atom in the reaction. The reaction was carried out by heating the reagents in a sealed vessel. At the end of the reaction the thiol was separated from the alcoholic solution by (i) the evaporation of the alcohol under reduced pressure and extraction of the thiol with ether, or (ii) addition of aqueous sodium hydroxide solution, evaporation to dryness under reduced pressure, acidification of the residue, and extraction of the thiol with ether, or (iii) addition of three volumes of water to the alcoholic solution, removal of the thiol that separated, followed by extraction of the remaining thiol with ether. The ether solution of the thiol was dried over anhydrous sodium sulphate, filtered, and then evaporated under reduced pressure. Each thiol was then redistilled until its purity, determined by iodine titration, reached a maximum. It was sometimes found that a thiol was difficult to purify by distillation. In such a case it was dissolved in ethanol, aqueous sodium hydroxide solution was added, the solution was evaporated to dryness under reduced pressure, and the thiol was liberated from the residue by acidification; it was then extracted with ether and purified by the method described above.

Preparation of Ammonium Hydrosulphide

This reagent was prepared by the method of Thomas and Riding (17). A stock solution of ammoniacal alcohol was obtained by bubbling ammonia gas (dried by passage over quicklime) through ethanol until a concentration of

50 to 60 gm. of ammonia per litre of solution was obtained. The concentration of ammonia in the solution was determined by titrating aliquot portions of the solution with hydrochloric acid, using methyl orange as indicator. Hydrogen sulphide, dried by passage over anhydrous calcium chloride, was passed through small portions of the ammoniacal ethanol at 0° C. Glistening white crystals formed which rapidly turned yellow, probably owing to the formation of polysulphides. The crystals were separated by filtration. Both the filtrate and a solution of the crystals were analysed by the titration of aliquot portions with hydrochloric acid and with iodine solution. It was found that analyses of the filtrate from the suspension of ammonium hydrosulphide in ethanol showed that the value of the ratio $NH_3 : H_2S$ was about 1.8, which corresponded to a solution containing $NH_4SH : 4(NH_4)_2S$. For a solution of the crystals the value of the ratio $NH_3 : H_2S$ was about 1.2, which corresponded to a solution containing $4NH_4SH : (NH_4)_2S$. The crystals were therefore used in the preparation of the thiols. They were added to ethanol at 0° C. in a glass pressure flask of 200 ml. capacity so that the volume of the suspension was 100 ml. The suspension was analysed for its ammonium hydrosulphide content and the halide was added in an amount such that there were two molecules of hydrosulphide for each halogen atom present. The flask was closed with a rubber stopper, which was then wired in position.

Preparation of Sodium Hydrosulphide

This reagent was prepared by the action of hydrogen sulphide on sodium hydroxide or sodium ethoxide in ethanol. After the theoretical amount of hydrogen sulphide had been absorbed, the solution was cooled to 0° C. and an excess of hydrogen sulphide was passed through. The advantage of using sodium ethoxide lay in the fact that an anhydrous solution of sodium hydrosulphide was obtained. Most of the thiol preparations in which sodium hydrosulphide was used were carried out in bombs of 650 and 1600 ml. capacity. Each bomb was provided with a gas valve for releasing the pressure previous to removing the contents of the bomb.

Determination of the Thiol Content of Preparations

The thiol content of the preparations was determined by titration with iodine solution in the following manner. A sample of about 0.05 gm. of the thiol was weighed accurately into a small glass cup, which was then dropped into 95% ethanol in a conical flask. The contents of the flask was shaken until all the thiol was dissolved in the ethanol. Iodine solution (0.1 *N*) was then run in slowly until a faint yellow colour remained. By means of this method it was possible to obtain duplicate values that did not differ by more than 0.5%. The iodine solution was standardized against sodium thiosulphate solution immediately before use.

Determination of Sulphur

A micro-Carius method was used to determine the sulphur content of the thiols. The procedure was based on that described by Niederl, Baum, McCoy, and Kuck (9).

Determination of Specific Gravity

The specific gravity of each thiol was determined in duplicate at 20° C., using pycnometers of approximately 0.6 ml. capacity, blown from tubing of 3 mm. inside diameter.

Experimental

In order to illustrate the methods used in the present work on the synthesis of thiols, the preparation of 1,2-dimercaptoethane from sodium hydrosulphide and that of 1,2-dimercaptopropane from ammonium hydrosulphide are described in detail.

1,2-Dimercaptoethane

Sodium hydroxide (40.0 gm.) was dissolved in ethanol (400 ml.) and converted to sodium hydrosulphide by the method described above. 1,2-Dibromoethane (47.0 gm.) was added and the solution was sealed in a bomb of 650 ml. capacity and heated at 30° C. for seven days and at 60° C. for four hours. The ethanol solution was filtered, three volumes of water were added to the filtrate, and the oil that separated was removed. The filtrate was made acid to Congo red with concentrated hydrochloric acid and was extracted with ether. The oil was combined with the ether extract and dried over anhydrous sodium sulphate. The ether was evaporated and the product was distilled under reduced pressure, b.p. 46° to 47° C. (16 mm.), 43° to 44° C. (14 mm.), sp.gr.$^{20}_{20}$ 1.124, yield 17%, purity 98.5% by iodine titration. Calc. for $C_2H_6S_2$: C, 25.49; H, 6.42; S, 68.10%. Found: C, 25.42; H, 6.58; S. 68.42%.

1,2-Dimercaptopropane

Preparation I. 3-Bromopropene (8.89 gm.) was added to 100 ml. of a suspension of ammonium hydrosulphide (15.0 gm.) in ethanol in a 200 ml. glass pressure flask. The flask was sealed and heated at 80° C. for eight hours. The contents of the flask was then filtered. The residue was dissolved in water and extracted with ether. To the filtrate, 30 ml. of 10 *N* sodium hydroxide was added. The solution was distilled under reduced pressure in order to remove the solvent and the residue was cooled to 0° C. and made acid to Congo red with concentrated hydrochloric acid. A pale-yellow oil separated. This was removed and the residue was extracted with ether. These ether extracts and the oil were combined with the ether extracts of the filtered reaction mixture and dried over anhydrous sodium sulphate. The ether was evaporated, the product was distilled, b.p. 59° C. (24 mm.), 49° to 50° C. (17 mm.), and 2.37 gm. (30% yield) of a colourless oil was obtained, sp.gr.$^{20}_{20}$ 1.061, the purity of which was 100% by iodine titration. Calc. for $C_3H_8S_2$: C, 33.28; H, 7.45%. Found: C, 33.86; H, 7.60%.

A comparison of the boiling point and specific gravity of this compound with those of 1,2- and 1,3-dimercaptopropane made from the dihalogen compounds shows that it was the 1,2-isomer that was obtained in the above preparation. A molecule of hydrogen sulphide was thus introduced into an unsaturated molecule by the action of ammonium hydrosulphide under pressure. The mode of addition was 'normal' according to an extension of Markownikoff's rule.

Preparation II. Sodium hydrosulphide was prepared from sodium hydroxide (80.0 gm.) in 1000 ml. of ethanol. 1,2-Dibromopropane (103.5 gm.) was added and the solution was heated at 25° C. for five days. The product was obtained by the addition of three volumes of water to the reaction mixture and was distilled under reduced pressure, b.p. 51° to 52° C. (17 mm.), sp. gr. $^{20}_{20}$ 1.063, yield 32%, purity 97% by iodine titration. Calc. for $C_3H_8S_2$: C, 33.28; H, 7.45; S, 59.27%. Found: C, 33.16; H, 7.69; S, 58.68%.

1,3-Dimercaptopropane

Preparation I. 1,3-Dibromopropane (14.6 gm.) was added to 100 ml. of a suspension of ammonium hydrosulphide (15 gm.) in ethanol and the solution was heated at 70° C. for eight hours. The product obtained from half of the ethanol solution by formation of the sodium mercaptide weighed 1.55 gm. The product obtained from the other half of the ethanol solution by the addition of three volumes of water weighed 3.02 gm. The two samples of the product were combined and distilled under reduced pressure, b.p. 57° C. (12 mm.), sp.gr.$^{20}_{20}$ 1.080, yield 20%, purity 99.5% by iodine titration. Calc. for $C_3H_8S_2$: C, 33.28; H, 7.45%. Found: C, 33.88; H, 7.67%.

Preparation II. Sodium hydroxide (40.0 gm.) was converted to sodium hydrosulphide in 500 ml. of ethanol. 1,3-Dibromopropane (50.5 gm.) was added and the solution was heated at 30° C. for seven days. The thiol was obtained by the addition of three volumes of water to the ethanol solution and was distilled under reduced pressure, b.p. 94° C. (60 mm.), 64° to 65° C. (15 mm.), sp.gr.$^{20}_{20}$ 1.081, yield 53%, purity 96.5% by iodine titration. Calc. for $C_3H_8S_2$: C, 33.28; H, 7.45; S, 59.27%. Found: C, 33.64; H, 7.58; S, 59.69%.

1,2,3-Trimercaptopropane

Preparation I. 1,2,3-Tribromopropane (14.0 gm.) was added to 15 gm. of ammonium hydrosulphide in 100 ml. of ethanol and the mixture was heated at 60° C. for 12 hr. The thiol was obtained by the addition of three volumes of water to the ethanol solution and was distilled under reduced pressure and 0.72 gm. (10% yield) was obtained, purity 97% by iodine titration. Calc. for $C_3H_8S_3$: C, 25.68; H, 5.75%. Found: C, 26.18; H, 5.75%.

Preparation II. Sodium hydrosulphide was prepared from sodium hydroxide (80.0 gm.) in 1000 ml. of ethanol. 1,2,3-Tribromopropane (140 gm.) was added and the solution was heated at 60° C. for six hours. The product was obtained by the addition of three volumes of water to the reaction mixture and was distilled under reduced pressure, b.p. 60° C. (0.40 mm.), 54° C. (0.18 mm.), 50° to 52° C. (0.045 mm.), sp.gr.$^{20}_{20}$ 1.233, yield 43%, purity 98% by iodine titration. The product was difficult to distil. Calc. for $C_3H_8S_3$: C, 25.68; H, 5.75; S, 68.60%. Found: C, 25.51; H, 5.80; S, 67.76%.

1,2-Dimercapto-n-butane

Preparation I. Sodium metal (16.0 gm.) was dissolved in 400 ml. of ethanol and converted to sodium hydrosulphide and this was precipitated by the addition of ether. Sodium hydrosulphide (32 gm.) and 1,2-dichloro-*n*-butane (12.0 gm.) were added to 400 ml. of ethanol and heated at 80° C. for 12 hr. The thiol was obtained through the formation of the sodium mercaptide and was distilled under reduced pressure, b.p. 77° C. (28 mm.), 49° C. (5 mm.), sp.gr.$^{20}_{20}$ 1.039, yield 25%, purity 98% by iodine titration. Calc. for $C_4H_{10}S_2$: C, 39.27; H, 8.24%. Found: C, 39.30; H, 8.22%.

Preparation II. Sodium hydrosulphide was prepared from sodium hydroxide (40.0 gm.) in 500 ml. of ethanol. 1,2-Dichloro-*n*-butane (31.7 gm.) was added and the solution was heated at 25° to 30° C. for seven days. The thiol was obtained by the addition of three volumes of water to the reaction mixture and was distilled under reduced pressure, b.p. 58° C. (13 mm.), yield 22%. The product was purified by conversion to the sodium mercaptide and by repeated distillation. The purity was 96% by iodine titration. Calc. for $C_4H_{10}S_2$: C, 39.27; H, 8.24; S, 52.7%. Found: C, 39.31; H, 8.03; S, 51.65%.

2,2′-Dimercaptoethyl ether

Preparation I. 2,2′-Dichloroethyl ether (11.2 gm.) was added to 100 ml. of a suspension of ammonium hydrosulphide (16.0 gm.) in ethanol and the mixture was heated at 80° C. for 12 hr. The solvent was removed by evaporation under reduced pressure, and the product was extracted with ether and distilled under reduced pressure, b.p. 53° to 54° C. (0.05 mm.), sp.gr.$^{20}_{20}$ 1.127, yield 35%, purity 100% by iodine titration. Calc. for $C_4H_{10}OS_2$: C, 34.73; H, 7.29%. Found: C, 34.90; H, 7.32%.

Preparation II. Sodium hydrosulphide was prepared from sodium hydroxide (40.0 gm.) in 500 ml. of ethanol. 2,2′-Dichloroethyl ether (35.7 gm.) was added and the solution was heated at 30° C. for seven days. The solution was made acid to Congo red by the addition of hydrochloric acid, filtered, and the solvent was evaporated under reduced pressure. The product was extracted with ether and distilled under reduced pressure and 6.8 gm. of thiol (20% yield) was obtained. The compound was purified by formation of the sodium mercaptide. The purity was 99% by iodine titration. Calc. for $C_4H_{10}OS_2$: C, 34.73; H, 7.29; S, 46.39%. Found: C, 34.98; H, 7.42; S, 46.79%.

3,3′-Dimercaptopropyl ether

Ammonium hydrosulphide (14.8 gm.) and 3,3′-dichloropropyl ether (12.5 gm.) were heated in 100 ml. of ethanol at 70° C. for five hours. The thiol was obtained by the addition of three volumes of water to the ethanol solution and was distilled under reduced pressure, b.p. 62° to 64° C. (0.125 mm.), sp.gr.$^{20}_{20}$ 1.055, yield 47%, purity 100% by iodine titration. Calc. for $C_6H_{14}OS_2$: C, 43.32; H, 8.49; S, 38.59%. Found: C, 43.04; H, 8.31; S, 38.70%.

2,2′-Dimercaptoisopropyl ether

Sodium hydroxide (80.0 gm.) was dissolved in 1000 ml. of ethanol and converted to sodium hydrosulphide. 2,2′-Dichloroisopropyl ether (85.5 gm.) was added and the solution was heated at 30° C. for 14 days and at 60° C. for six hours. The product was separated by the addition of three volumes of water to the reaction mixture and was purified by formation of the sodium mercaptide and by distillation under reduced pressure, b.p. 52° to 54° C. (0.55 mm.), sp. gr. $^{20}_{20}$ 1.053, yield 11%, purity 99% by iodine titration. Calc. for $C_6H_{14}OS_2$: C, 43.32; H, 8.49; S, 38.59%. Found: C, 42.78; H, 8.37; S, 38.58%.

1,3-Dimercapto-2-propanol

Preparation I. 1,3-Dibromo-2-propanol (10.7 gm.) was added to 10 gm. of ammonium hydrosulphide in 100 ml. of ethanol and the mixture was heated at 80° C. for 12 hr. The product was obtained by evaporating the alcohol under reduced pressure and extracting the residue with ether. The compound was distilled under reduced pressure, b.p. 55° C. (0.040 mm.), yield 26%, purity 95% by iodine titration. Calc. for $C_3H_8OS_2$: C, 28.98; H, 6.49%. Found: C, 29.37; H, 6.25%.

Preparation II. Sodium metal (23.0 gm.) was dissolved in 400 ml. of ethanol and converted to sodium hydrosulphide. 1,3-Dibromo-2-propanol (54.5 gm.) was added and the solution was heated at 30° C. for 72 hr. and at 60° C. for two hours. Glacial acetic acid (60.0 gm.) was added and the solvent was removed by evaporation under reduced pressure. Water was added to dissolve the solid material and ammonium hydroxide was added until the solution was alkaline to litmus. The product was extracted with ether and distilled under reduced pressure, b.p. 60° C. (0.060 mm.), sp.gr.$^{20}_{20}$ 1.241, yield 40%, purity 95% by iodine titration. Calc. for $C_3H_8OS_2$: C, 28.98; H, 6.49; S, 51.63%. Found: C, 29.33; H, 6.58; S, 52.49%.

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SYNTHESIS OF AMINO ACIDS FROM SUBSTITUTED CYANOACETIC ESTERS. 4-ALKYL-3-AMINOPYRAZOLONES[1]

By Paul E. Gagnon[2], Kenneth Savard[3], Roger Gaudry[4], and Edwin M. Richardson[5]

Abstract

Four α-amino acids, namely, norleucine, isoleucine, methionine, and S-benzylhomocysteine, have been prepared from the corresponding alkylcyanoacetic esters. Methionine has been obtained in excellent yield.

The intermediate alkylcyanoacethydrazides formed 4-alkyl-3-aminopyrazolones. Four members of this new series, 4-*n*-butyl-, 4-*sec*-butyl-, 4-(β-methylthiolethyl)-, and 4-(β-benzylthiolethyl)-3-aminopyrazolones are described and their ultraviolet absorption spectra given.

The following compounds have also been isolated: ethyl α-cyano-γ-methylthiolbutyrate, ethyl α-cyano-γ-benzylthiolbutyrate, α-cyano-*n*-caprohydrazide, isopropylidene α-cyano-*n*-caprohydrazide, anisal α-cyano-β-methylvalerhydrazide, anisal α-cyano-γ-methylthiolbutyrhydrazide, and anisal α-cyano-γ-benzylthiolbutyrhydrazide.

Introduction

The application of the Curtius reaction to the synthesis of amino acids was first suggested by Darapsky and Hillers (10) in 1915 by their synthesis of glycine. It was not until 1936 that the proposed method received further attention when Darapsky (9), starting from alkylcyanoacetic esters, successfully prepared, with fairly good yields, α-amino-*n*-valeric acid, α-aminoisoamylacetic acid, and *dl*-leucine.

Later, Gagnon, Gaudry, and King (13) obtained, by the same method, α-amino-δ-phenoxyvaleric acid and the three natural amino acids, *dl*-tyrosine, *dl*-phenylalanine and *dl*-valine. The high yields (50 and 60%) obtained by these authors in the synthesis of the last two amino acids, together with the fact that ether groups are not affected by the conditions of the Darapsky method, indicated the possibility of wider applicability of the Curtius reaction to the synthesis of amino acids.

The present study was undertaken primarily to extend the Darapsky application of the Curtius reaction to the preparation of sulphur-containing amino acids, in particular methionine. Before this was begun, experience was gained by first preparing the two isomeric amino acids, norleucine (VII, R = *n*-butyl) and isoleucine (VII, R = *sec*-butyl); the method was then

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Contribution from the Department of Chemistry, Laval University, Quebec, and the Research and Biological Laboratories of Ayerst, McKenna, and Harrison, Limited, Montée St. Laurent, Montreal. This paper constitutes part of a thesis submitted to the Graduate School, Laval University, in partial fulfilment of the requirements for the degree of Doctor of Science.

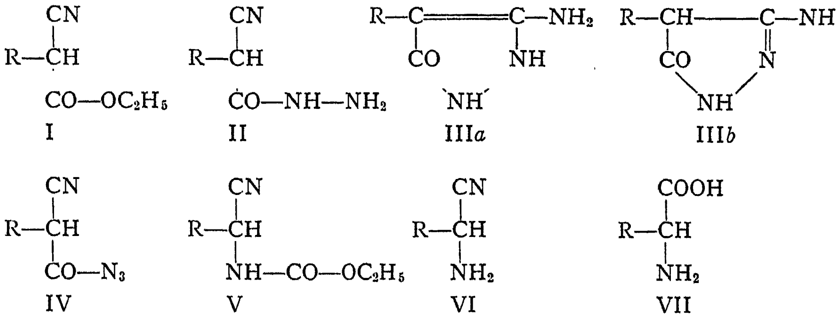
[2] *Professor of Chemistry and President of the Graduate School.*

[3] *Formerly graduate student, holder of a Shawinigan Chemicals Limited Research Scholarship; and later, research chemist, Ayerst, McKenna, and Harrison Limited.*

[4] *Assistant Professor of Biochemistry, Department of Biochemistry of the Faculty of Medicine, Laval University.*

[5] *Research chemist, Ayerst, McKenna, and Harrison Limited.*

successfully applied to the synthesis of methionine (VII, R = β-methylthiolethyl) and S-benzylhomocysteine (VII, R = β-benzylthiolethyl).



R = *n*-butyl, (CH_3-CH_2-CH_2-CH_2-); *s*-butyl, (CH_3-CH_2-$CH(CH_3)$-); β-methylthiolethyl, (CH_3-S-CH_2-CH_2-); β-benzylthiolethyl, (C_6H_5-CH_2-S-CH_2-CH_2-).

As starting materials, the alkylcyanoacetic esters (I) were prepared by the condensation of alkyl halides with ethyl cyanoacetate; when alkyl chlorides were employed, better yields were obtained by the addition of potassium iodide to the reaction medium (31). The formation of the hydrazides (II) took place quantitatively at room temperature; only one of the products, α-cyano-*n*-caprohydrazide (II, R = *n*-butyl) was obtained as a low melting solid, the remainder were viscous liquids and were identified by their crystalline condensation products with anisaldehyde.

The crude alkylcyanoacethydrazides, on standing for some time, underwent transformation to the corresponding 4-alkyl-3-aminopyrazolones (III*a*, III*b*), the rate of the reaction being increased when sodium hydroxide was used as a catalyst (14, 29).

Ultraviolet absorption determinations on these compounds revealed that the principal absorption peaks were in close agreement with those characteristic of the pyrazolone ring (3, 4, 25).

This is the first time that 3-aminopyrazolones substituted *only* in the 4-position are described. 3-Aminopyrazolones substituted in positions 1 and 2 have already been reported (26-30).

The conversion of the hydrazides through the azides (IV) to the urethanes (V) took place smoothly without loss. These intermediate products were viscous liquids and were not isolated. Hydrolysis of the urethanes, giving *dl*-norleucine in 45% yield and *dl*-isoleucine in 54% yield, was accomplished with aqueous hydrochloric acid (20%). The identification of the latter amino acid as the copper salt revealed the possibility that the two racemates, *dl*-isoleucine and *dl*-alloisoleucine, might be easily separated because of the difference in solubility of the copper salts; this point will be studied further and reported on in a subsequent publication.

The hydrolysis in 20% hydrochloric acid of the sulphur-containing urethane (V, R = β-methylthiolethyl) leading to methionine gave a very poor yield of the amino acid, and was accompanied by excessive tar formation. This has previously been noted by Barger and Coyne (2) in the hydrolysis of the corresponding amino nitrile (VI). Although the choice of hydrolysing agents is limited by the instability of methionine towards sulphuric, hydrobromic, and hydriodic acids (5), a variety of reagents were tested; these included alcoholic sodium hydroxide, fused baryta (11), and anhydrous alcoholic hydrochloric acid followed by mild hydrolysis (imino ether method). Yields of methionine ranging from 12 to 45% were obtained. Best results were given by a mixture of formic acid, hydrochloric acid, and water. This reagent, described by Carter, Stevens, and Ney (6) and successfully used by others (23), completely dissolved the urethane at the boiling point, and, after six hours of refluxing, gave an excellent yield of *dl*-methionine corresponding to 85% conversion of the urethane; longer periods of refluxing (24 hr.) caused considerable destruction (43%) of the product. The yield of *dl*-methionine calculated from ethyl α-cyano-γ-methylthiolbutyrate (I, R = β-methylthiolethyl) was 73%, and is the highest reported so far in the various amino acid syntheses by the Darapsky method.

The mixture of formic acid, hydrochloric acid, and water was employed in the preparation of S-benzylhomocysteine.

Experimental*

Ethyl Alkylcyanoacetates (I)

To a warm solution of sodium ethoxide (0.6 mole of sodium and 350 to 500 ml. of absolute ethyl alcohol), freshly distilled ethyl cyanoacetate (1.2 moles) and later the alkyl chloride or bromide (0.6 mole) were added and the solution was refluxed on a water-bath for the required length of time. After the excess of alcohol had been removed by distillation, the residual sludge was poured into cold water. The dark red oily layer formed was separated and the aqueous layer extracted several times with ether. The oily layer and the ethereal extracts were combined, and the solution dried over anhydrous sodium sulphate. The ether was removed by distillation and the residue fractionated. The properties and yields of the ethyl alkylcyanoacetates are given in Table I.

Alkylcyanoacethydrazides (II)

The ethyl alkylcyanoacetate (0.06 mole) and aqueous hydrazine hydrate (85%, 0.06 mole) were mixed and dissolved in absolute ethyl alcohol. The solution was allowed to stand at room temperature overnight and then freed from solvent in a vacuum desiccator. The reaction was quantitative. The residual viscous products could not be induced to crystallize, except α-cyano-*n*-caprohydrazide, and were used without further purification. A small quantity of α-cyano-*n*-caprohydrazide was recrystallized from ether (below room temperature) and gave colourless crystals: m.p. 49° to 51° C. Calc. for $C_7H_{13}ON_3$: N, 27.10%. Found: N, 27.20%. The alkylcyanoacethydrazides were identified by condensation with acetone or anisaldehyde in the usual way. The properties of the products obtained are given in Table II.

All melting points are uncorrected.

TABLE I

ETHYL ALKYLCYANOACETATES, $RCH(CN)COOC_2H_5$

Alkyl group, R	Starting material	Time of reaction, hr.	Yield, %	B.p., ° C.	n_D^{25}
n-Butyl[a]	CH_3–CH_2–CH_2–CH_2–Br	20	76	93.5–96 (3.5 mm.)	1.4246
s-Butyl[b]	CH_3–CH_2–$CH(CH_3)$–Br	20	59	92.5–93.5 (5.0 mm.)	1.4267
β-Methylthiolethyl[c]	CH_3–S–CH_2–CH_2–Cl[d, e]	12	54	131–133 (5.0 mm.)	1.4725
β-Benzylthiolethyl[f]	C_6H_5–CH_2–S–CH_2–CH_2–Cl[d, g]	12	49	169–170 (0.5 mm.)	1.5331

[a] *Ref. (1, 15);* [b] *Ref. (1,8).* [c] *Calc. for* $C_8H_{13}O_2NS$ *: N, 7.53; S, 17.22%. Found: N, 7.53; S, 17.10%.* [d] *Potassium iodide (2.0 gm.) added to the reaction mixture.* [e] *Prepared from β-hydroxyethyl methyl sulphide kindly supplied by Dr. Eric Stiller of Wyeth Inc. Philadelphia.* [f] *Calc. for* $C_{14}H_{17}O_2NS$*; N, 5.33; S, 12.20%. Found: N, 5.33; S, 12.00%.* [g] *Prepared according to the procedure of Patterson and du Vigneaud (22).*

TABLE II

CONDENSATION PRODUCTS OF ALKYLCYANOACETHYDRAZIDES

R′-CH(CN)-CO-NH-N = CR″R‴

R′	R″	R‴	Solvent	M.p., ° C.	Formula	Analysis, %			
						Nitrogen		Sulphur	
						Calc.	Found	Calc.	Found
n-Butyl	Methyl	Methyl	Ether	79– 80.5	$C_{10}H_{17}ON_3$	21.53	21.56	—	—
s-Butyl	H	*p*-Methoxyphenyl	EtOH	140–141	$C_{15}H_{19}O_2N_3$	15.39	15.41	—	—
β-Methylthiolethyl	H	*p*-Methoxyphenyl	MeOH	135–137	$C_{14}H_{17}O_2N_3S$	14.43	14.17	11.01	11.00
β-Benzylthiolethyl	H	*p*-Methoxyphenyl	MeOH	127–128	$C_{20}H_{21}O_2N_3S$	11.44	11.19	8.73	8.55

Amino Acids (VII)

The crude alkylcyanoacethydrazides were converted through the azides to the corresponding urethanes in the manner previously outlined (9, 13). The urethanes were viscous liquids obtained in quantitative yields except in the case of the urethane leading to S-benzylhomocysteine, where the yield was 26%. The hydrolysing medium was added to the crude urethane and the mixture refluxed. After filtration, the solution was evaporated to dryness *in vacuo*. The excess of acid was removed by repeatedly dissolving the residue in water and evaporating to dryness *in vacuo*. The residue was then dissolved in the minimum quantity of hot water and decolorized with charcoal (norite). The clear solution was adjusted to the isoelectric point of the amino acid with ammonium hydroxide, and the resulting precipitate dissolved by heating to the boiling point. An equal volume of ethyl alcohol was added and the solution cooled for a few hours. Glistening crystals were formed. They were filtered, washed with cold water followed by alcohol, and dried. Concentration of the filtrate to small volume and treatment with alcohol yielded a second crop. Recrystallization from water–ethyl-alcohol yielded the pure product, which gave a positive ninhydrin test.

The properties and yields of the amino acids obtained by this procedure are listed in Table III, together with the properties of the derivatives prepared.

TABLE III

AMINO ACIDS

Compound	Hydrolysis medium	Time, hr.	Yield,[a] %	Formula	Nitrogen, %		Derivative
					Calc.	Found	
dl-Norleucine	20% HCl	22	45	$C_6H_{13}O_2N$	10.68	10.83	Hydantoin, m.p. 138° to 139°C.[b]
dl-Isoleucine	20% HCl	22	54	$C_6H_{13}O_2N$	10.68	10.91	Cu salt[c]
dl-S-Benzylhomocysteine[d]	Mixed acids[e]	10	9	$C_{11}H_{14}O_2NS$	6.22	5.98	—
dl-Methionine[f]	Mixed acids[e]	6 24	73 58	$C_5H_{11}O_2NS$[g]	9.39	9.31	Hydantoin, m.p. 115° to 117° C.[h]

[a] *Calculated from the ethyl alkylcyanoacetate.* [b] *Ref. (18).* [c] *Calc. for* $Cu(C_6H_{12}O_2N)_2$; *N, 8.66%. Found: methyl alcohol soluble salt, N, 8.48%; methyl alcohol insoluble salt, N, 8.66%.* [d] *M.p. 194° to 196° C.* [e] *Equal portions by volume of concentrated hydrochloric acid, 85% formic acid, and water.* [f] *McCarthy–Sullivan test (20) was positive.* [g] *Calc. S, 21.49%. Found: S, 21.23%.* [h] *Ref. (16).*

The copper salt of *dl*-isoleucine was prepared according to the method of Town (24). Extraction of the dry salt with methyl alcohol revealed the presence of two components, one very soluble in methyl alcohol and the other slightly soluble, probably *dl*-isoleucine and *dl*-alloisoleucine.

4-Alkyl-3-aminopyrazolones (III)

The crude alkylcyanoacethydrazides, treated with sodium hydroxide according to the method of Hepner and Fajersztejn (14), gave rise to the corresponding 4-alkyl-3-aminopyrazolones, which were difficult to separate from the sodium acetate present.

The crude alkylcyanoacethydrazides, on standing at room temperature for several weeks, *also* yielded pyrazolones quantitatively. These were more readily purified by recrystallization from ethyl acetate or a mixture of this solvent and ether. The resulting colourless products were identified by mixed melting point determinations and analysis. One sample, analysed by the ordinary Kjeldahl method, gave figures corresponding to only one nitrogen atom per mole, whereas after pretreatment with hydriodic acid (12), figures corresponding to the three nitrogen atoms were obtained. These 4-alkyl-3-

aminopyrazolones, the properties of which are listed in Table IV, were employed for the ultraviolet absorption determinations.

The absorption measurements were made on a Beckman Quartz Spectrophotometer Model DU (7), using a hydrogen discharge tube as light source. All measurements were made in stoppered quartz cells of 1.000 ± 0.002 cm. length. Redistilled absolute methyl alcohol was employed throughout the determinations and solutions were prepared by progressive dilution of a sample weighed on a microbalance. Initial measurements of each sample were made in the spectral range 4000 to 2200 Å, at intervals of 20 Å; in the region of the absorption maxima and minima, readings were made at intervals of 10 Å. Subsequent measurements were limited to the range 3200 to 2200 Å when it was apparent that the compounds studied possessed no significant absorption in the region above 3200 Å. A spectral band width of 10 Å was employed at all wave-lengths.

The values recorded in Table IV and Fig. 1 were calculated in terms of E_m, where E_m is molar extinction coefficient, defined by the equation

$$E_m = \frac{M}{c.d} \cdot \log_{10} I_0/I$$

M = the molecular weight of the solute,

c = the concentration of solute in milligrams per millilitre,

d = the cell thickness (length of light path) in cm.,

I_0 = the intensity of the incident light,

I = the intensity of the emergent light. The value of the extinction coefficient, I_0/I, is read directly from the photometer drum of the instrument.

A close inspection of the curves shown in Fig. 1 reveals the fact that the spectra of 4-(β-methylthiolethyl)-3-aminopyrazolone and 4-(β-benzylthiolethyl)-3-aminopyrazolone are almost identical, the slight deviation of the latter being due to the benzene ring which, 'insulated' from the conjugated system, contributes additively to the absorption (17). The secondary maxima present in the spectra of 4-*n*-butyl-3-aminopyrazolone and, to a lesser degree (as an inflection point only), 4-*sec*-butyl-3-aminopyrazolone is in the region of absorption of α, β-unsaturated ketones (17, 32); this would indicate that at least under the conditions of the measurements these compounds exist in both structural forms III*a* and III*b*. A further indication is the melting point range of several of these products. Biquard and Grammaticakis, by preparing 1-phenyl-2,3,4-trimethylpyrazolone, which can exist only as the form corresponding to III*a*, and 1-phenyl-3,4,4-trimethylpyrazolone corresponding to structure III*b*, have shown that pyrazolones having these two structures exhibit distinctly different absorption spectra (4). As a result of their work, it may be concluded that in alcoholic solution, 4-*n*-butyl- and 4-*sec*-butyl-3-aminopyrazolones exist as both structural forms III*a* and III*b*, while 4-(β-methylthiolethyl)- and 4-(β-benzylthiolethyl)-3-aminopyrazolones exist solely as structural form III*b*.

TABLE IV

4-ALKYL-3-AMINOPYRAZOLONES

3-Aminopyrazolones	Formula	M.p., °C.	Mol. wt.[a]		Analysis, %								Ultraviolet absorption maxima	
					Carbon		Hydrogen		Nitrogen[b]		Sulphur			
			Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Å	E_m
4-*n*-Butyl	$C_7H_{13}ON_3$	128–130	155	158	—	—	—	—	27.10	26.94	—	—	2480[c] 2820[c]	8450 3620
4-*s*-Butyl	$C_7H_{13}ON_3$	145–146	155	157	54.15	54.45	8.44	8.42	27.10	26.75	—	—	2480[c] (2720)[d]	4750 3520
4-(β-Methylthiolethyl)	$C_6H_{11}ON_3S$	121–122	173	197	41.58	41.43	6.40	6.00	24.27	24.36	18.51	18.61	2450[c]	13100
4-(β-Benzylthiolethyl)	$C_{12}H_{15}ON_3S$	109–111	249	208	—	—	—	—	16.87	16.95	12.86	12.59	2450	13000

[a] *In acetone, method of Menzies and Wright (21).* [b] *Hydriodic acid digestion prior to Kjeldahl determination (12).* [c] *Absorption spectra of product prepared with sodium hydroxide was identical.* [d] *Inflection point.*

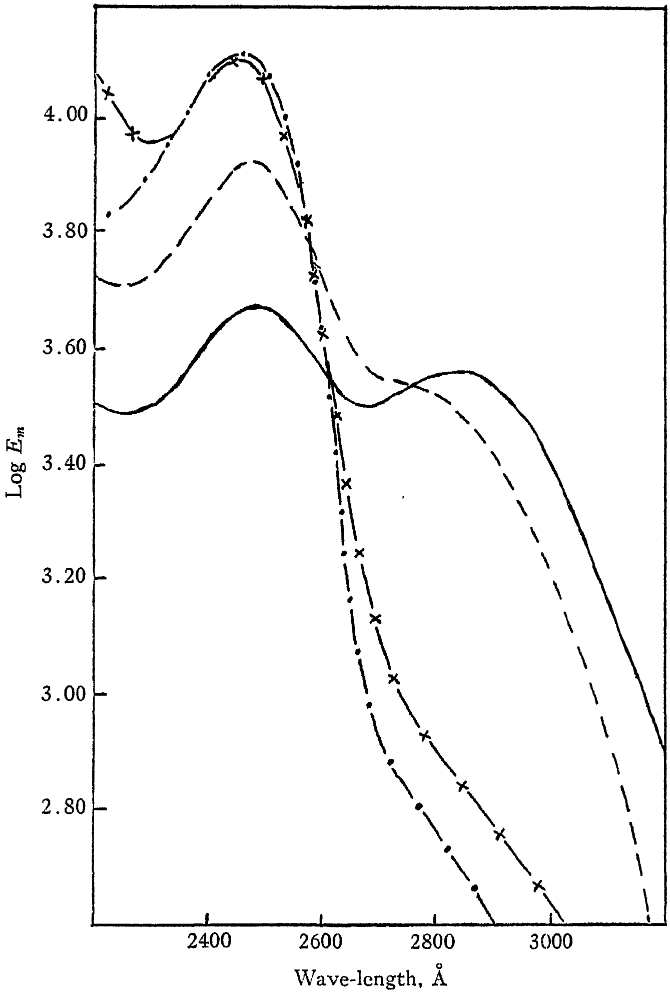


FIG. 1.

——————— *4-n-Butyl-3-aminopyrazolone*
— — — — — — *4-s-Butyl-3-aminopyrazolone*
— · — · — *4-(β-Methylthiolethyl)-3-aminopyrazolone*
—×—×— *4-(β-Benzylthiolethyl)-3-aminopyrazolone*

Acknowledgment

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THE REACTION OF β,β'-DICHLORODIETHYL SULPHIDE WITH PROTEINS[1]

BY E. GORDON YOUNG[2] AND ROBERTA B. CAMPBELL[3]

Abstract

The reaction of β,β'-dichlorodiethyl sulphide with various proteins and their constituents has been tested under relatively mild conditions. Most reactions have been carried out in aqueous media at 25° C., usually in the presence of sodium chloride. The rate of disappearance of mustard has been followed iodimetrically as an index of the reaction.

No reaction could be demonstrated with the prolamins, zein and gliadin, in ethanol. There was a definite reaction with keratin of human skin in which a 24% increment in total sulphur occurred and a more doubtful one with keratein from human hair.

The most notable reaction took place with yeast and thymus nucleoproteins in which increases of 250 and 156% in sulphur occurred, respectively. Combination of mustard with both the protein and nucleic acid portions was demonstrated. The extent of these reactions is indicated in terms of milligrams of mustard per gram of substrate as follows: yeast nucleoprotein, 216; thymus nucleoprotein, 47; salmine, 47; globin, 22; yeast nucleic acid, 126. The purines, adenine and guanine, were found to combine readily with mustard at 25° C., forming thiazans. No reaction could be demonstrated with uracil or thiamine.

These experiments have led us to the conclusion that one of the major effects of mustard in its physiological action is the combination and precipitation of the nucleoproteins of the cell, thus inhibiting natural processes of cellular regeneration.

The purpose of the investigation to be described was to analyse the reaction between β,β'-dichlorodiethyl sulphide and various types of proteins. It was hoped to discover something of the kinetics of the reaction, especially as applied to the proteins of the skin, to prepare reaction products and to obtain information as to the nature of the reaction, as a guide to a better understanding of the mechanism of action of mustard on human skin.

Previous investigations have established reactions with many amino acids (5, 16). These reactions resulted in α–N-substitution products, similar to those with amines. Evidence for a reaction with proteins has been based largely on the formation of a product with increased sulphur content (3) or on specific immunological properties. In a few instances the disappearance of reactive radicals in the protein molecule, such as α-amino, free carboxyl, sulphhydryl and phenolic, has been measured as an index of the reaction or the stability of the compound formed.

Experimental

This work began in February 1942, and was concluded in July 1945. It has involved experiments with prolamins, keratins from human skin and

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[2] *Professor of Biochemistry.*

[3] *Graduate student.*

hair, yeast and thymus nucleoproteins and their constituent parts, including salmine, nucleic acid, adenine, guanine and uracil, and in addition a few observations on globin and thiamine. After the development for our purposes of a satisfactory quantitative method for the estimation of mustard, the general procedure has been essentially the same.

General Procedure

The substrate was dissolved, completely when possible, usually in an aqueous medium in low concentration. The reaction was carried on in a large water-bath maintained at 25° C. ± 1°. The reaction mixture was stirred mechanically at such a speed as not to incorporate any air in the liquid. The medium was maintained between pH 7 and 8, determined electrometrically, by the addition of sodium bicarbonate, carbonate, or hydroxide as required. Mustard was added in small quantities as a 10% solution in absolute ethanol, at such intervals as was indicated by the determination of free mustard in the reaction mixture. The rate of disappearance of mustard was followed by iodimetric titration as given below. When the reaction appeared complete the substrate was precipitated, fractionated, purified carefully, dehydrated, and finally desiccated over phosphorus pentoxide at 61° C. in a pistol desiccator. Microchemical elementary analysis for sulphur has been used as confirmatory evidence of reaction.

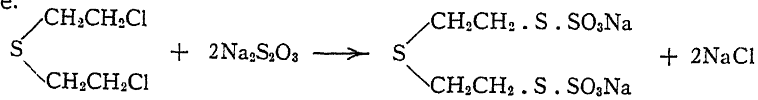
In many instances sodium chloride was added to the medium at 3 to 5% concentration to depress the rate of hydrolysis of mustard (19). We have found the rate depressed to about one-eighth of that in distilled water under our experimental conditions. The only disadvantage to this procedure is the subsequent difficulty in separation if the reaction product is readily soluble.

Microanalysis of sulphur was done by catalytic combustion followed by gravimetric estimation as barium sulphate. The nitrogen was determined either by micro-Dumas or by digestion with hydriodic acid under pressure at 200° C. for two hours, followed by micro-Kjeldahl estimation.

All results are expressed on an ash-free basis.

Iodimetric Estimation of Mustard

At intervals during the reaction, 1 ml. of the reaction mixture was pipetted into a 50 ml. Erlenmeyer flask, mixed with 2 ml. of sodium thiosulphate (0.01 *N*) and heated for 10 min. at 60° C. The excess thiosulphate was determined by titration with 0.01 *N* iodine in a microburette, with 0.5% soluble starch as indicator, in a neutral or slightly acid medium. The method depends upon the reaction of any free mustard with sodium thiosulphate to form sodium dithiosulphatyl diethyl sulphide and titration of excess thiosulphate.



$$S(CH_2CH_2Cl)_2 + 2Na_2S_2O_3 \longrightarrow S(CH_2CH_2 . S . SO_3Na)_2 + 2NaCl$$

In this method it was necessary to rule out by control test any reaction of the iodine or thiosulphate with the substrate. It was found that 1 ml. of thiosulphate (0.01 *N*) was equivalent to 0.804 mgm. of mustard. Theoretically it should have reacted with 0.795 mgm. The method was reproducible to ± 10% approximately.

Materials

Two samples of mustard were used in the course of this investigation. One, obtained from Dr. George Wright, University of Toronto, had a slight yellowish colour and a melting point of 12.3° C. as against the usually accepted figure of 13° to 14° C. (20). The other, supplied by Dr. Robert MacIntosh, McGill University, melted at 12.4° C.

The methods of preparation or purification of the various substrates will be described in their separate sections below.

Prolamins

Zein

Zein was chosen first as substrate because of its solubility in common with mustard in ethanol and because of the slow rate of hydrolysis of mustard under these conditions. A commercial sample of zein (Pfanstiehl) was purified by a modification of the method of Osborne and Clapp (18) and of Dill and Alsberg (9). Zein (3.135 gm.) in 100 ml. of ethanol (90% *v/v*) was treated with 0.50 ml. of mustard ($\approx$ 0.637 gm.) and 1.00 gm. of sodium bicarbonate and the mixture heated at 60° C. for 18 hr. A blank was first run in the same manner to determine the rate of hydrolysis of mustard under these conditions. The results are shown in Table I. It is evident that decomposition in 90% ethanol at 20° C. is slow but is almost complete in 24 hr. at 60° C.

TABLE I

RATE OF HYDROLYSIS OF MUSTARD IN 90% ETHANOL

Time	Temp., ° C.	Hydrolysis, %
6 days	20	14.6
8 hr.	60	61.2
16 hr.	60	79.3
25 hr.	60	94.0

The H^+ ion concentration changed from pH 8.52 to 2.12. Excess mustard was removed by petrol extraction and the reaction product was isolated and purified exhaustively. On microanalysis the following values were obtained: 1.05% S and 15.9% N in control and 1.05% S and 10.9% N in the reaction product.

There would thus seem to be no evidence of combination between zein and mustard despite the time available for a reaction. The loss in total nitrogen is appreciable and may be explained by hydrolysis of amide linkages during the course of the reaction. Zein is remarkable because of its very low content of the basic amino acids. It possesses, however, a high content of dicarboxylic acids but the carboxyl radicals appear to be in amide linkage. Cohn, Berggren, and Hendry (6) remark that "the extremely small concentration both of acid and basic groups, and the very low solubility of zein in water, and in dilute solutions of acids and alkalis characterize zein as a very inert protein, more inert than any other that we have thus far investigated."

The action of an alcoholic solution of the reaction product was tested by application of a concentrated solution to the skin of very young mice. It induced a very slight erythema without induration, so that the result was considered negative.

Gliadin

A sample was prepared by the method of Osborne and Harris as modified by Dill and Alsberg (9) and Dill (8). Gliadin (3.009 gm.) was dissolved in 100 ml. of ethanol (80% *v/v*), and 0.5 ml. of mustard (≈ 0.637 gm.) added and 1.00 gm. of sodium bicarbonate. The reaction mixture was heated in an all-glass apparatus under reflux at 60° C. for 23 hr. A control without the gliadin was also carried out as a guide to the rate of hydrolysis of mustard under these conditions. The results are given in Table II.

TABLE II

RATE OF REACTION IN 80% ETHANOL AT 60° C.

Control		Gliadin	
Time, hr.	Hydrolysis, %	Time, hr.	Hydrolysis, %
2.0	44.1	2.0	48.8
4.2	55.9	5.0	72.2
7.2	81.0	7.0	76.8
15.2	97.6	12.0	81.4
—	—	23.0	100.0

The pH was 8.96 at the start and 9.28 at the end of the reaction. The reaction product was isolated and purified by repeated precipitation in absolute acetone and resolution in 70% ethanol. The microanalyses showed 1.37% S and 17.9% N in the control and 1.28% S and 17.2% N in the reaction product.

As with zein there is no evidence of a combination of gliadin with mustard on the basis of an increase in the sulphur content. Gliadin possesses few diamino acids but has a high content of glutamic acid (43.77%) in amide linkage (amide N, 5.2%). It is probable that the prolamins do not possess the requisite radicals, such as the sulphhydryl, to react with mustard, or that an aqueous medium is required.

Keratins

A closer approach to physiological conditions was therefore attempted. Several specimens of human skin from abdomen and leg were defatted, dried, and comminuted in a Wiley mill to pass a No. 20 mesh sieve. A white fibrous powder was obtained.

A sample of human hair was washed with water, defatted with ether, and converted into keratein by way of increasing the available sulphhydryl groupings and the solubility. The product was a light grayish powder.

Keratin from Human Skin

A portion (1 gm.) of the mixed proteins of human skin was suspended in 200 ml. of sodium carbonate (0.1 *M*), and 0.5 ml. of mustard was added to the reaction mixture during a period of three hours, at 25° C. The solid remaining was washed thoroughly with 0.1 *M* sodium carbonate, water, aqueous acetone (50%), and absolute acetone. It was finally extracted with acetone in a Soxhlet apparatus for 48 hr. Results of microanalysis are given in Table III.

TABLE III

ANALYSES OF SKIN PROTEINS

——		I, %	II, %	Mean, %
Skin proteins (control)	S	0.38	0.53	0.46
	N	15.15	15.21	15.18
	Ash	1.46	1.37	1.42
Skin proteins–mustard	S	0.49	0.65	0.57
	N	15.49	15.68	15.59
	Ash	0.42	0.38	0.40

The increase in the mean for the sulphur content was therefore 0.11, or 24% over the content of the control as indication of mustard fixation. This is equivalent to 5.5 mgm. per gm. of keratin. The discrepancies in the duplicates should, however, be taken into consideration.

Keratin from Human Hair

Washed defatted hair (50 gm.) was treated with sodium thioglycolate at pH 12 according to the procedure of Goddard and Michaelis (11). It was dissolved in 0.1% sodium hydroxide and precipitated with acetic acid. The keratein was washed with absolute ethanol and then absolute ether. Finally it was dried in a vacuum desiccator over calcium chloride at 37° C. for two days. This material was ground in a Wiley mill to pass through a No. 40 mesh sieve. A light gray powder (5 gm.) was obtained. The material was free from thioglycolic acid as shown by the cobalt test. It had an ash content of 1.6%.

A portion (1.0 gm.) was dissolved in 200 ml. of 0.1 *M* sodium carbonate and treated at 25° C. with 1.2 ml. of mustard dissolved in 25 ml. of absolute ethanol, added as 0.1 ml. at 30-min. intervals over a period of six hours. During the reaction the pH dropped from 10 to 8. A precipitate appeared in about three hours. This was centrifuged down, washed with acetone and thoroughly dried. Microanalyses showed 4.64% S in the control and 4.82% S in the reaction product. The increment of sulphur was thus 0.18, equivalent to 10 mgm. of mustard per gm. of protein.

Nucleoproteins

Yeast Nucleoprotein

A specimen was prepared from fresh commercial baker's yeast by extracting with distilled water, 0.5% sodium carbonate, and 1 *M* sodium chloride. On acidification of the extracts the nucleoprotein precipitated at pH 4.0 from distilled water, at 5.7 from the carbonate extract, and at 4.7 from the saline extract. The precipitates were combined and dissolved in dilute ammonia at pH 8, reprecipitated and dried.

A portion (1 gm.) of the dried precipitate was dissolved in 0.1 *M* sodium bicarbonate at pH 8. To this was added a total of 6 ml. of mustard in absolute ethanol over a period of six hours. A precipitate, which proved to be insoluble in dilute acid and base, appeared during the second hour. It was thoroughly extracted before drying and analysis (Table IV).

TABLE IV

ANALYSES OF YEAST NUCLEOPROTEINS

——		I, %	II, %	Mean, %
Nucleoprotein (control)	S	1.68	1.76	1.72
	N	9.18	9.56	9.37
	Ash	7.48	7.69	7.59
Nucleoprotein–mustard	S	5.99	6.07	6.04
	N	10.40	10.77	10.19
	Ash	0.51	0.42	0.47

The results of the analysis show a marked increase of 250% in the sulphur content of the treated specimen. It is equivalent to the reaction of 216 mgm. per gm. of nucleoprotein.

Thymus Nucleoprotein

A sample of nucleoprotein from desiccated thymus (Armour) was prepared by the method of Mirsky and Pollister (17).

A portion (1.4 gm.) dissolved in 5.8% sodium chloride (1 *M*) was exposed to the action of 0.4 gm. of mustard at pH 7-8 and 25° C. for 11 hr. A precipitate appeared in 1.5 hr. Mustard was added about every 30 min. as it disappeared from solution. The precipitate was centrifuged off, washed in aqueous acetone, and dehydrated in absolute acetone. A second fraction settled out after dilution from the original reaction mixture on standing. This was dehydrated in ethanol. Microanalyses for sulphur are given in Table V.

TABLE V

ANALYSES OF THYMUS NUCLEOPROTEINS

——	I, %	II, %	Mean, %
Thymus nucleoprotein (control)	0.56	0.65	0.61
Nucleoprotein–mustard, 1st fraction	1.65	1.47	1.56
Nucleoprotein–mustard, 2nd fraction	1.67	1.45	1.55

The ash contents were 7.09, 7.66, and 4.7%, respectively. The two fractions isolated were taken to be the same compound. *There is a marked increase in bound sulphur between treated and untreated specimens of 0.95 or 156%, comparable with the reaction noted with yeast nucleoprotein.* This is equivalent to 4.7 mgm. of mustard per gm. of protein.

Constituents of Nucleoprotein

Our attention was next directed to an analysis of the reaction with the various constituents of nucleoprotein. To this end we have studied the effect of mustard on globin, salmine, nucleic acid, and finally purines and pyrimidines.

Globin

The method of preparation from dog's blood was that of Anson and Mirsky (1) and the product was a dark brown powder, soluble in aqueous solvents. The reaction was carried out with 0.5 gm. dissolved in 200 ml. of 3% sodium chloride acidified with acetic acid to pH 3, and two additions of 0.25 ml. of mustard over a period of 11 hr. The reaction product formed a precipitate on the addition of sodium hydroxide. This was dispersed readily in aqueous acetone and reprecipitated only under the influence of sodium chloride. It was washed in water and dehydrated by absolute ethanol. The following were the results on microanalysis: 0.67% S and 15.8% N in the control and 1.12% S and 15.3% N in the reaction product.

The reaction product isolated had a very high ash content which would reduce the accuracy of the estimation of total sulphur. However, there appeared to be a definite increment in total sulphur equivalent to 22 mgm. of mustard per gm. of protein. No further experiments were done with globin.

Salmine

A few grams of salmine sulphate (obtained from Connaught Laboratories, through the courtesy of Dr. D. A. Scott) was dissolved in water and all sulphate precipitated with a solution of barium chloride, leaving salmine chloride in solution. The free salmine was precipitated by adjusting the pH to 8.5 and adding ethanol (95%). The product was a white powder.

Salmine hydrochloride (1.5 gm.) was dissolved in 120 ml. of distilled water and treated with 0.8 gm. of mustard at 25° C. over a period of 30 hr. The pH was maintained at 8.0. The resulting solution was evaporated to small volume *in vacuo* and six volumes of acetone added. The flocculent precipitate settled out as an oil. Solution and precipitation were repeated and the product dried in the pistol desiccator to a light brownish powder. On microanalysis the following results were obtained: 0.00% S in control and 0.95% S in the reaction product.

There was therefore an increase of 0.95% of sulphur, equivalent to 47 mgm. of mustard per gm. of protein. Assuming a molecular weight of 3000 for salmine, 1 mole of mustard per mole of protein would be equivalent to 53 mgm. per gm., which corresponds with the result obtained.

Nucleic Acid

Yeast nucleic acid (Eastman) (10 gm.) was purified after the procedure of Baumann (2) and Steudel and Izumi (21). The nucleic acid precipitated between pH 3 and 1.5 at 0° C. and was dehydrated with absolute ethanol and ether, yielding 6.8 gm. The biuret test was negative.

The reaction with mustard was carried out at 25° C. in 100 ml. of a solution containing 5% sodium chloride, 1% sodium bicarbonate, and 1% nucleic acid, over a period of six hours. Mustard was added twice as 0.25 ml. The initial pH was 8.20 and the final 8.15. The product was isolated in two fractions after extraction with petrol (i) precipitated at pH 4 to 1.4, and (ii) precipitated at 1.4 with ethanol. The precipitates were dehydrated with ethanol and acetone. The first fraction was a slightly yellow solid resembling the original. The second was a snow-white powder. The microanalytical results are given in Table VI.

TABLE VI

ANALYSES OF YEAST NUCLEIC ACID

——		I, %	II, %	Mean, %
Nucleic acid (control)	S	0	0	0
Nucleic acid–H (1st)	S	2.45	2.60	2.52
	Ash	21.6	20.9	21.3
Nucleic acid–H (2nd)	S	0.77	0.61	0.69
	Ash	22.2	21.3	21.8

There was thus an appreciable fixation of sulphur in the first fraction, comparable with the result obtained with yeast nucleoprotein, and much higher than that with globin. This is equivalent to 126 mgm. of mustard per gm. of product. These results led us to try the effect of mustard on adenine and guanine.

Guanine

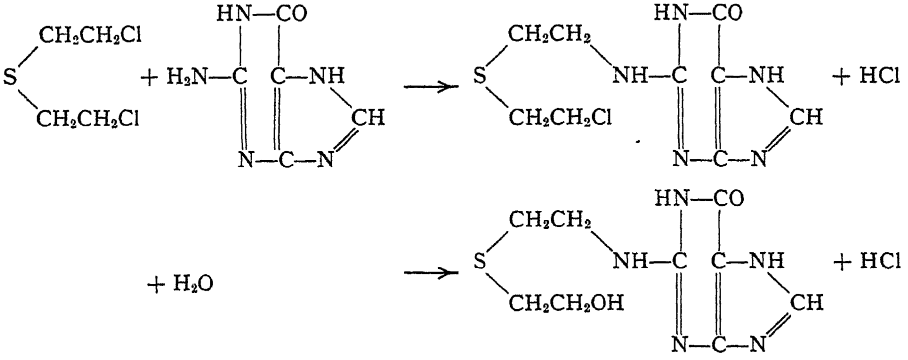
A specimen of guanine was prepared according to the method of Hunter and Hlynka (13) from yeast nucleic acid. Owing to its slight solubility it was necessary to alter the usual procedure.

Guanine (0.5 gm.) was dissolved in 1000 ml. of 0.1% sodium hydroxide at 45° C. and 0.2 ml. of mustard in ethanol was added at intervals of 30 min. up to a total of 2.5 ml. The pH was maintained between 7.5 and 8.0 during a reaction lasting about 10 hr. There was evidence by iodimetric titration of the rapid disappearance of mustard during the first few hours.

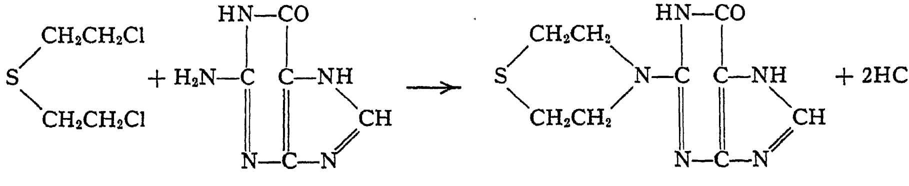
The reaction mixtures were neutralized with hydrochloric acid and concentrated *in vacuo* at 45° C. The residue was extracted repeatedly with benzine and finally the mixture was evaporated to dryness *in vacuo*. The slightly yellowish residue was removed from the flask with a small amount of water. A deep yellow solution and a white solid resulted. The solution was evaporated *in vacuo* until sodium chloride crystals separated out. The clear yellow mother liquor was evaporated to dryness and the residue extracted with 95% ethanol. The extract was treated with an excess of redistilled ether. A white precipitate, which turned yellow on standing and proved very hygroscopic (G-2), was obtained. It was examined microscopically and tested for sodium chloride but none was found present.

The insoluble portion from the reaction mixture was redissolved in water made alkaline (pH 8). This solution was concentrated and treated with excess of 95% ethanol to the formation of a white precipitate. This was next taken up in absolute ethanol and precipitated with anhydrous ether. The precipitate was very hygroscopic and had an ash content of 54.8% (G-3). The microanalytical results for total sulphur were as follows, calculated on an ash-free basis: (G-2) 11.7% S and (G-3) 11.8% S.

It was concluded from these results that a definite reaction had taken place and that the two fractions isolated were the same compound. The product differed from guanine in its greater solubility in water and alcohol, and its crystalline form. The most probable combination would be with the amino group in position 2. If the following reactions had taken place the products would have had a content of sulphur of (1) 12.5%, (2) 13.5%.



(1)



(2)

Owing to the hygroscopic character of the products obtained it is not possible to decide which reaction took place, but the probable character of the reaction is indicated by the agreement in the sulphur content, calculated and determined. This is in contrast with any further fixation of mustard molecules by the guanine, such as on positions 1 or 7, to give products with even higher content of sulphur.

Adenine

A specimen of adenine was prepared according to the method of Hunter and Hlynka (13) from yeast nucleic acid along with the guanine.

Adenine (0.4 gm.) was dissolved in 250 ml. of 0.25% acetic acid and 6 ml. of mustard added over a period of 16 hr. A constant pH of about 6 was maintained by adding small amounts of dilute sodium hydroxide. The reaction mixture was concentrated *in vacuo* and a precipitate formed. It was dissolved in water and reprecipitated by adding one volume of ethanol and two volumes of ether. The material had an ash content of 36.1% but possessed sufficient sulphur, 0.32%, to indicate that a reaction with adenine had taken place although not as rapidly or completely as with guanine.

Uracil

Owing to the limited solubility of uracil, a specimen of potassium uracil was prepared by the procedure of Johnson and Clapp (14) from uracil made from urea and malic acid by the synthesis of Davidson and Baudisch (7).

Uracil (1 gm.), dissolved in 200 ml. of 5% sodium chloride, was treated with 0.4 ml. of mustard added in small amounts over a period of six hours at 25° C. The initial pH of 9.45 fell to 7.8 during this interval. The residual mustard was allowed to hydrolyse and the solution was concentrated *in vacuo* to dryness. The residue was extracted with 95% ethanol, and the extract evaporated to dryness, and washed with absolute ethanol. There was no evidence of a reaction iodimetrically and the product obtained contained no sulphur. This is perhaps not surprising owing to the absence of any amino group in the pyrimidine molecule.

Cytosine

The result with uracil led us to attempt a reaction with cytosine. One effort of synthesis from uracil by the method of Hilbert and Johnson (12) was unsuccessful owing to the small yield obtained.

Thiamine

The biological importance of thiamine and its pyrimidine character suggested a trial of the reaction of this substance with mustard.

Thiamine hydrochloride (Merck) (1 gm.) was dissolved in 60 ml. of water and treated with 0.2 ml. of mustard at 25° C. for six hours; pH 7.0 was maintained by additions of dilute sodium hydroxide. The reaction product was isolated by adding equal volumes of alcohol and ether. It was redissolved in alcohol and again precipitated with ether. No evidence of a reaction was apparent iodimetrically and the sulphur analysis of the white crystalline precipitate showed a value of 6.11% S in contrast to the control at 9.32% S. The value for sulphur in pure thiamine is 9.53%. There was thus no evidence of a combination with mustard on the free amino group and the product was either impure or some decomposition of the original thiamine must have taken place.

Discussion

A summary of our results is presented in Table VII. It is apparent from all recent investigations that mustard is a highly reactive substance and capable of combination with amino acids and proteins, under more or less physiological conditions. Our work has shown that a greater amount of mustard is combined with nucleoprotein than with any other protein. We show further that this reaction is applicable to both cytoplasmic and nuclear nucleoproteins but especially to the former to the extent of a combination of 216 mgm. per gm. of protein. Further analysis of this reaction has established that both the protein and nucleic acid fractions are able to combine with mustard. With nucleic acid the reaction is monomolecular, equivalent to 126 mgm. of mustard per gm. of nucleic acid (theoretical, 111, to molecular weight of product of 1304). The reactive constituent of nucleic acid is shown here to be guanine with which mustard combines in equimolar proportions (S found 11.8% as against a theoretical 12.5%). It is not shown, however, that a similar reaction does take place with adenine or cytosine. The reaction would most probably occur by hydrogen substitution on the free amino radical. No reaction took place with thiamine, however, under our conditions.

TABLE VII

SUMMARY

Substrate	Sulphur, %			Ratio mustard : product, mgm. : gm.
	Initial	Final	Increment	
Zein	1.05	1.05	0.00	0
Gliadin	1.37	1.28	− 0.09	0
Keratin (skin)	0.46	0.57	+ 0.11	5.5
Keratein (hair)	4.64	4.82	+ 0.18	10
Nucleoprotein (yeast)	1.72	6.04	+ 4.32	216
Nuceloprotein (thymus)	0.61	1.56	+ 0.95	47
Globin	0.67	1.12	+ 0.45	22
Salmine	0.00	0.95	+ 0.95	47
Nucleic acid	0.00	2.52	+ 2.52	126
Guanine	0.00	11.73	+ 11.73	586
Adenine	0.00	0.32	+ 0.32	16

We have also shown that an equimolar combination between mustard and salmine takes place based on an assumed molecular weight of 3000 (47 mgm. of mustard per gm. of protein found, as against 53 mgm. theoretical). From these experiments with nucleoprotein, nucleic acid, and guanine, it would appear that more mustard molecules are bound to the protein portion than to the nucleic acid portion of the molecule.

Recent publications have shown the protein nature of hexokinase (15) and the role of guanine as a coenzyme in the phosphorylation of glucose in the hexokinase reaction (4). Dixon and Needham (10) have exp'ained the vesicant action of mustard on the basis of the inhibition of this reaction. It is possible therefore that the effect may be due to a reaction of mustard with guanine as shown above.

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5-HYDROXYQUINOLINE-8-CARBOXYLIC ACID—A COLORIMETRIC REAGENT FOR RUTHENIUM[1]

J. G. Breckenridge[2] and S. A. G. Singer[3]

Abstract

5-Aminoquinoline-8-carboxylic acid was prepared from 8-methylquinoline by nitration in the 5-position, oxidation of the methyl group to carboxyl, and reduction of the nitro group to amino. The 5-aminoquinoline-8-carboxylic acid was converted to 5-hydroxyquinoline-8-carboxylic acid through the diazonium salt. Some of the properties of the two new compounds were determined.

A transmission curve was established for solutions showing the colour developed by the reagent and ruthenium. The standard ruthenium solution used for this purpose contained the metal as it is obtained when distilled as the tetroxide and collected in hydrogen peroxide. Ruthenium in a solution as ammonium chlororuthenate could be determined from the same curve. One γ (1×10^{-6} gm.) of ruthenium in 50 ml. of solution may be quantitatively determined.

Introduction

Quinoline-8-carboxylic acid, a potential organic analytical reagent, has apparently not been extensively investigated except by Majumdar, who has published a paper concerning its use as a gravimetric reagent for copper (3) and has done some further work which will be published shortly (private communication). From preliminary tests in these laboratories it did not seem to be promising as a colorimetric reagent for metal ions, and it was decided to modify the nature of the compound by substitution and to examine the possibilities of the derivatives. The present paper deals with the synthesis of the 5-hydroxy derivative and its applicability as a colorimetric reagent for ruthenium, an element for which there has been no method of analysis by colorimetry available.

Part I

PREPARATION AND PROPERTIES OF 5-AMINOQUINOLINE-8-CARBOXYLIC ACID AND 5-HYDROXYQUINOLINE-8-CARBOXYLIC ACID

These compounds are not mentioned in the literature. 5-Nitroquinoline-8-carboxylic acid, which could easily be converted into 5-aminoquinoline-8-carboxylic acid, was prepared by Howitz and Nöther (2) from 8-methylquinoline by a series of five reactions, one of the intermediates being a very active vesicant. The authors have repeated these reactions successfully, but the over-all yield is very small (about 5% of theoretical) and the time required was considerable. Therefore another method of obtaining the acid from 8-methylquinoline had to be devised.

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[1] *Manuscript received July 3, 1946.*

Contribution from the Department of Chemical Engineering, University of Toronto, Toronto, Ont.

[2] *Professor.*

[3] *Research Assistant.*

Experimental

1. 5-Nitro-8-methylquinoline

This was prepared from 8-methylquinoline by the method of Noelting and Trautmann (4).

2. 5-Nitroquinoline-8-carboxylic acid

Thirty grams of 5-nitro-8-methylquinoline, 66 gm. of sodium bichromate dihydrate, and 150 ml. of water were boiled under a reflux condenser for five minutes. Ninety millilitres of concentrated sulphuric acid (sp. gr. 1.84) was added slowly to the boiling mixture, through the condenser. Care had to be taken to avoid violent spattering. The reddish-black mixture was refluxed for one hour, the colour changing to green. The solution was diluted to two litres with water, cooled, and 1 : 1 ammonium hydroxide was added until the greenish-brown chromium hydroxide began to precipitate. About 15 ml. of 6 *N* sulphuric acid was then added and the precipitate was filtered off and washed with four litres of water. The precipitate was suspended in 600 ml. of 1.5% sodium hydroxide solution and agitated violently for 15 min. The insoluble unchanged base was filtered off. The filtrate was neutralized with 6 *N* sulphuric acid, precipitating the white 5-nitroquinoline-8-carboxylic acid, which was filtered off. M.p. 209° to 213° C.* Net yield, 60% of theoretical.

3. 5-Aminoquinoline-8-carboxylic acid

An adaptation of the method of Dikshoorn (1) was used. Ten grams of 5-nitroquinoline-8-carboxylic acid and 100 ml. of 50% by volume aqueous acetic acid were boiled under a reflux condenser for five minutes. The solution was then cooled to 80° C., forming a semisolid white mass to which was added 8 gm. of iron powder. There was violent effervescence and the mass turned red. The reaction mixture was refluxed for half an hour, then shaken with 400 ml. of water and heated to 50° C. to dissolve the iron acetate. The solution was cooled and filtered. The filtrate was acidified with sulphuric acid, precipitating as the sulphate any amine that had dissolved. The precipitates of iron and the amine were separated from each other by recrystallization from 3½ litres of boiling water; yield, 60% of theoretical.

The amine formed long yellow needles, m.p. 271° to 272° C.* with decomposition, only slightly soluble in ethanol, benzene, cold water, dilute mineral acids (forming salts), soluble in boiling water and acetic acid. Found: C, 63.90, H, 4.21, N, 15.62%. Calc. for $C_{10}H_8N_2O_2$: C, 63.81, H, 4.28, N, 14.89%. The amine sulphate is a bright red solid, m.p. 244° C.* with decomposition, insoluble in dilute mineral acids, but soluble in concentrated mineral acids. The use of the amine as a reagent would be complicated by its insolubility in neutral and weakly acid solutions.

4. 5-Hydroxyquinoline-8-carboxylic acid

A solution of 5.7 gm. of 5-aminoquinoline-8-carboxylic acid, 5.7 gm. of anhydrous sodium carbonate and 21 gm. of sodium nitrite in 200 ml. of water was poured slowly with stirring into 500 ml. of boiling 2.5 *N* sulphuric acid solution. The resultant solution was cooled and ammonium hydroxide was added until a brown precipitate had formed, which was filtered off. The brown precipitate was recrystallized from 95% ethanol, giving light yellow crystals. Yield, 37% of theoretical. The compound begins to decompose at 226° C.* with partial sublimation. It is insoluble in cold water, cold ethanol, acetone, benzene, and soluble in boiling water, boiling ethanol, and pyridine. Found: C, 63.40, H, 3.64, N, 7.46%. Calc. for $C_{10}H_7NO_3$: C, 63.46, H, 3.75, N, 7.40%.

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* *Corrected.*

Part II

5-HYDROXYQUINOLINE-8-CARBOXYLIC ACID AS AN ANALYTICAL REAGENT

Experimental

A Qualitative Work

An aqueous solution of the sodium salt of 5-hydroxyquinoline-8-carboxylic acid was tested both cold and after boiling, with the following ions: Al^{+++}, NH_4^+, Sb^{+++}, Ba^{++}, Be^{++}, Bi^{+++}, Cd^{++}, Ce^{++}, Cr^{+++}, Co^{++}, Cu^{++}, Au^+, Fe^{++}, Fe^{+++}, Pb^{++}, Li^+, Mg^{++}, Mn^{++}, Hg^{++}, Hg^+, Ni^{++}, Pd^{++}, Pt^{+++}, Ru^{+++}, Ag^+, Sn^{++}, Sn^{++++}, Tl^{+++}, Th^{++++}, U^{++++++}, Zn^{++}, Zr^{++}, Ir, Rh, Os. Precipitates were obtained with many of the ions. These precipitates will be investigated in the future. Only iron and ruthenium gave highly coloured solutions, ferrous iron giving a dark green solution in the cold and after heating, and ferric iron giving a brownish-green solution after boiling. Ruthenium gave a very dark bluish-black solution after boiling. The ferrous iron colour was very intense at pH about 7, even in a solution containing only 4 to 8 parts of ferrous iron in 10 million. However, this colour is very weak below pH 1.4, where the ruthenium colour was developed for the quantitative work

The colour with ruthenium does not develop in the presence of nitric acid or nitrites, and is perceptibly weakened by the addition of hydrochloric acid.

B. Quantitative Work

The standard ruthenium solution for use in establishing the curves was prepared by distilling a standard solution of ammonium chlororuthenate in dilute hydrogen bromide, using the method of Rogers, Beamish, and Russell (5). The distillate was boiled with 50 ml. of 1 : 20 hydrobromic acid and diluted to one litre. Aliquots of this solution were taken to determine the various points. The distillation was done in duplicate, the curve obtained from the two distillations being shown in Fig. 2 for a 1 cm. cell and Fig. 3 for a 5 cm. cell.

The following procedure was used. The ruthenium solution was measured with a pipette into a 150 ml. beaker. If it had not been previously boiled with dilute hydrobromic acid, it was diluted to 50 ml., 2.5 ml. of 1 : 20 hydrobromic acid (1 ml. concentrated (42%) hydrobromic acid to 20 ml. water) was added, and the solution was boiled for 10 min. It was then cooled in running water. If the solution had been treated previously with hydrobromic acid, this treatment was omitted.

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* *Corrected.*

To this solution were added 5.0 ml. of 6 *N* sulphuric acid and 10 ml. of a 0.05% by weight solution of the sodium salt of the reagent (this solution was prepared by suspending 0.5 gm. of the reagent in one litre of water, adding 0.5 gm. of anhydrous sodium carbonate, heating to 40° C., and allowing to cool). The solution was boiled for five minutes, cooled in running water, and diluted with water to 50 ml. in a volumetric flask. Transmission readings were taken at once.

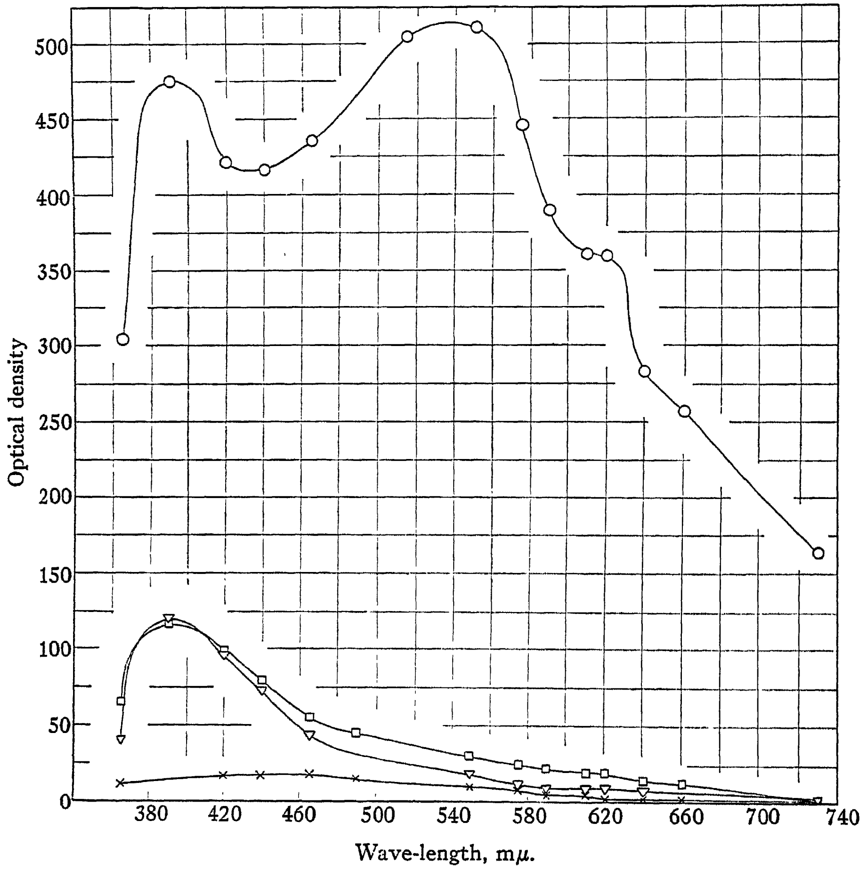

FIG. 1. *Colour absorption curve.*
○ *204 γ/50 ml. ruthenium.*
□ *400 γ/50 ml. iridium.*
▽ *400 γ/50 ml. platinum.*
× *500 γ/50 ml. osmium.*

The absorption at various wave-lengths was obtained using the above procedure, the optical density being determined with filters of various wave-lengths in a Klett-Summerson colorimeter, against a blank that had been

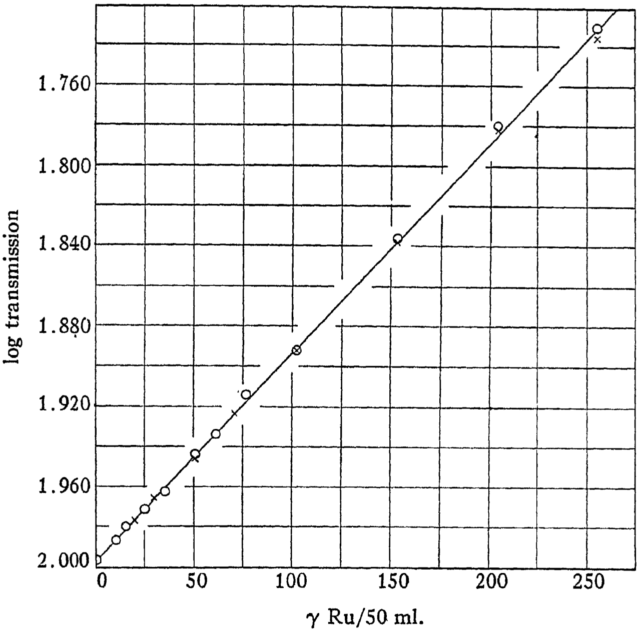

FIG. 2. *Application of Beer's law, 1 cm. cell.*

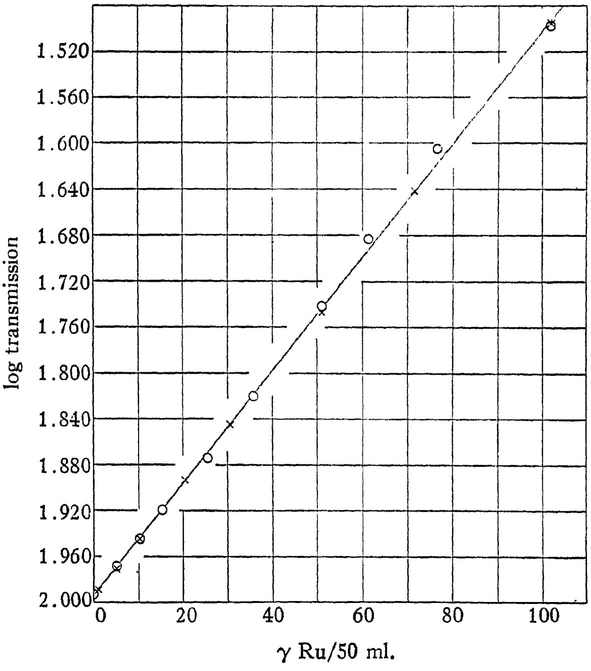

FIG. 3. *Application of Beer's law., 5 cm. cell.*

prepared in the same way but that contained no ruthenium. The curve was determined for solutions containing ruthenium, osmium, iridium, and platinum, respectively (Fig. 1). Ruthenium is difficult to separate from these metals except by distillation. The only methods at present available for determining ruthenium are based on separation by distillation. The shape of these curves indicates that for ruthenium determinations a combination of Wratten filters No. 66 and No. 15, with a Cenco–Sheard–Sanford photelometer would be suitable, and 1- or 5-cm. cells. The true blank has a slight absorption which is not constant, but changes over several hours. Hence a water blank was used, the transmission of water being taken as 100%.

Results and Discussion

The curve obtained indicates that the solutions formed with ruthenium and 5-hydroxyquinoline-8-carboxylic acid obey Beer's law. The curve does not pass through the origin because a water blank was used. The graph could be extended to higher concentrations, as it has been determined for ammonium chlororuthenate up to 750 γ in 50 ml., but this is unnecessary as aliquots may be taken to bring the amount of ruthenium present into the range 0 to 250 γ per 50 ml. The limiting perceptible concentration, using the Cenco–Sheard–Sanford photelometer with the filters as noted above, is 1 γ in 50 ml., or 1 part in 50 million. In a solution containing only the other platinum metals in small amounts and ruthenium the latter may be determined within a few per cent by this method, without a distillation (Fig. 1).

A 10 mgm. distillation was used as a standard, as Rogers, Beamish, and Russell (5) state that the method is quantitative within 1% under the most unfavourable circumstances, and is usually much better than this.

The hydroxyl group, as well as the carboxyl group, must affect the reaction, because the authors determined that quinoline-8-carboxylic acid, 5-aminoquinoline-8-carboxylic acid, and 5-hydroxyquinoline do not give any colour with ruthenium, under similar conditions.

The properties of precipitates given with 5-hydroxyquinoline-8-carboxylic acid and some of the metals will be investigated further. More derivatives of quinoline-8-carboxylic acid are being made and their effectiveness as analytical reagents will be investigated.

Acknowledgments

The authors thank Prof. F. E. Beamish of the University of Toronto, for his advice and co-operation, and Mr. R. E. Thiers, for performing the ruthenium distillations.

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PRODUCTION AND PROPERTIES OF 2,3-BUTANEDIOL

XVII. FERMENTATION OF GLUCOSE BY STRAINS OF *BACILLUS SUBTILIS*[1]

By A. C. Blackwood[2], A. C. Neish[3], W. E. Brown[3], and G. A. Ledingham[4]

Abstract

Under aerobic conditions both the Marburg and Ford types of *Bacillus subtilis* dissimilate glucose, giving carbon dioxide, acetoin, and 2,3-butanediol as the main products, and small amounts of glycerol and acetic, formic, lactic, and *n*-butyric acids. The Ford type cultures dissimilate the sugar more rapidly and also give a small amount of ethanol.

Under anaerobic conditions Marburg type cultures will not ferment glucose while the Ford type cultures dissimilate it as rapidly as they do under aerobic conditions. Some strains give 2,3-butanediol, glycerol, and carbon dioxide as the major products while others give chiefly lactic acid. As much as 86% and as little as 8% of the glucose was converted to 2,3-butanediol plus glycerol. The 2,3-butanediol was a mixture of 65% *meso-* and 35% *levo-*isomers, while the lactic acid was approximately 90% *dextro-*isomer in most cases.

It is suggested that the Ford type deserves separate species rank.

Introduction

Preliminary studies on the dissimilation of glucose by a Ford strain of *Bacillus subtilis* (7) indicated that the fermentation followed the equation:

$$3C_6H_{12}O_6 \longrightarrow 2CH_3.CHOH.CHOH.CH_3 + 2CH_2OH.CHOH.CH_2OH + 4CO_2.$$

Owing to the production of some ethanol and lactic acid, only 78% of the glucose was dissimilated according to this equation. Since these studies were all conducted with one strain of *B. subtilis* it appeared worth while to assess a number of strains to see how closely the theoretical yields could be approached.

In addition to the fermentation studies, detailed bacteriological investigations were made on a large number of *Bacillus* isolates. Most of these were isolated locally but several strains were obtained from other laboratories interested in the taxonomy of this genus. The morphological and biochemical characteristics of the Marburg and Ford type strains were compared.

Experimental

Cultures and Media

A number of *Bacillus subtilis* cultures were obtained and the fermentation characteristics were determined on the following:

B_2—A Ford strain secured from Dr. Lochhead, Central Experimental Farm, Ottawa, number 246 in his collection and used in the previous study (7).

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[2] *Bacteriologist, Industrial Utilization Investigations.*

[3] *Biochemist, Industrial Utilization Investigations.*

[4] *Mycologist, Industrial Utilization Investigations.*

B_5—One of Ford's original cultures secured from Dr. N. R. Smith, U.S.D.A., Washington, and numbered 243 in his collection.

B_7—Secured from Dr. N. R. Smith and numbered 329 in his collection.

B_{42}—Marburg strain, number 6051 secured from the American Type Culture Collection.

B_{43}—Marburg strain secured from Dr. I. C. Gunsalus, Cornell University, Ithaca, N.Y., and numbered C_4 in his collection.

B_{44}—Ford strain secured from Dr. I. C. Gunsalus and numbered S_8 in his collection.

In addition a large number of *Bacillus* cultures were isolated and 169 were identified as *Bacillus subtilis* according to a scheme suggested by Dr. N. R. Smith (11). Carbon balances were obtained mainly under anaerobic conditions for the above named cultures and for 27 of the isolates. Only those cultures that fermented glucose rapidly were used.

In preparing the medium used, 5.0% c.p. glucose and 0.5% yeast extract (Difco) were sterilized together and, after cooling, sterile salts solution (potassium monohydrogen phosphate (0.05%), potassium dihydrogen phosphate (0.05%), magnesium sulphate heptahydrate (0.02%)) was added. A weighed amount (about 1%) of sterile calcium carbonate was added at the time of inoculation with 7.5% of a 24 hr. inoculum grown at 37° C. Preliminary experiments showed that the salts added at the above levels were sufficient. Lower levels of yeast extract gave slower fermentations.

*Analysis and Identification of Products**

Analytical methods for determining the yield of products were the same as described previously (7) except that hydrochloric acid was used to acidify the culture, and the bacteria and proteins were precipitated with zinc hydroxide according to the method of Somogyi (12).

In order that other cultures might be more easily assessed a further group was analysed only for the following products; 2,3-butanediol, glycerol, ethanol, and lactic acid. The rate of fermentation was measured daily by recording the time taken by the carbon dioxide given off to neutralize a standard amount of sodium hydroxide to the phenolphthalein end-point. When fermentation had ceased (as evidenced by a long decolorization time) the amount of residual glucose, 2,3-butanediol, glycerol, ethanol, and lactic acid was determined as follows. The solutions were cleared with zinc hydroxide. Glucose was determined by the method of Underkofler *et al.* (13) and ethanol by distillation and dichromate oxidation. The amount of lactic acid was estimated by a modification of Hillig's (2) colorimetric method. If glucose was present in more than trace amounts it was removed with copper lime treatment and the amount of 2,3-butanediol and glycerol was determined with periodate. The formic acid found on periodate oxidation and the amount of periodate reduced were determined according to Shupe's procedure

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**A mimeographed bulletin has been prepared that contains full details of all the analytical methods. A copy of this is available for anyone requesting it.*

(10) except that 0.1 *M* sodium periodate was used instead of 0.01 *M* potassium periodate and excess periodate was determined by the method of Rappaport *et al.* (8).

The isolation and identification of the fermentation products were carried out by the same methods as previously described (7) except for lactic acid. The relative amounts of *dextro-* and *levo*-lactic acid were determined by preparing the silver salt of lactic benzimidazole according to the method of Moore *et al.* (6).

Results

Identification of Cultures

A detailed investigation of the morphological and biochemical characteristics of the cultures isolated in this laboratory and identified as *Bacillus subtilis* has shown that they are similar to the *subtilis* group described by Gibson (1), Knaysi and Gunsalus (3), Lamanna (4), and others. The organism is described as a motile, mesophilic, aerobic rod with a diameter less than 0.9μ. The cells from glucose nutrient agar stain evenly and are Gram-positive at 24 hr. in nutrient broth. The sporangia are not distinctly bulged and are oval to cylindrical with central to terminal thin-walled spores. The organism is V.P. positive, hydrolyzes starch, gelatin and casein and reduces nitrate to nitrite. When ammonium salts are used as the nitrogen source, acid but no gas is produced from glucose, xylose, arabinose, fructose, sucrose, maltose, glycerol, and mannitol but not from lactose. Growth on nutrient agar slopes and plates is abundant, dull, and wrinkled. Often the growth tends to adhere to the agar and, if the agar is moist, to spread rapidly.

However, considerable variation was noted among the isolates. Some difficulties were encountered in determing the characteristics of the sporangium and some isolates were first segregated because the sporangium tended to be swollen with a terminal spore. Repeated tests, however, showed that this was a variable characteristic and certainly not clearly defined. Thus, these cultures were included in the *subtilis* group. Some definite differences in colony form were noted but as reported by Gibson (1) these also were found to vary with time. The largest groups of true variants were those that did not produce diastase (16 cultures). These resemble *B. subtilis* in all other respects and were separated from the *B. pumilus* cultures, which do not produce diastase but also do not reduce nitrates to nitrites. A few cultures, contrary to type, produced some acid from lactose. Growth occurred over a wide temperature range but all fermentations were carried out at 30° to 37° C.

In the study of the rate of fermentation of glucose under mildly aerobic conditions it soon became apparent that there was a division into two rather distinct groups. The Marburg type cultures utilized the carbohydrate slowly while the Ford type cultures dissimilated the sugar quite rapidly. This difference is shown in Fig. 1. Most of the cultures were easily separated into the two groups and the rest were roughly segregated on the basis of other tests. A preliminary comparison with the results of morphological and other biochemical tests shows that this division between the Marburg and Ford types is probably valid. Further investigation is necessary to prove the value of this proposed method of separation although both Gibson (1) and Knaysi and Gunsalus (3) use growth and production of carbon dioxide under anaerobic conditions as definite criteria.

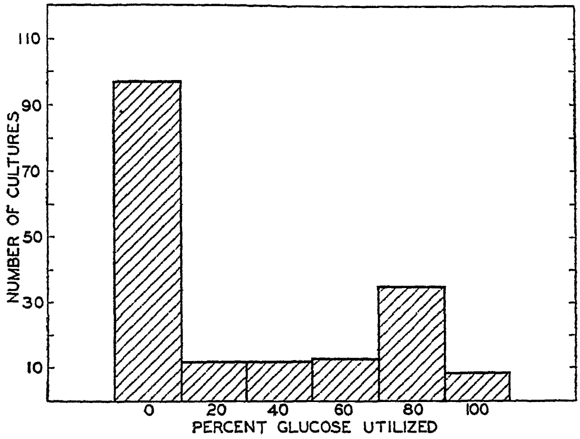

FIG. 1. *Glucose utilized by Bacillus subtilis at 37° C. in five days. The bacteria were grown aerobically on medium containing 5% glucose, 0.5% yeast extract, and 1% calcium carbonate.*

Dissimilation of Glucose by Bacillus subtilis (Marburg Type)

Although the Marburg type cultures fermented glucose very slowly it was desirable to determine the products so that a comparison might be made. The rate of carbon dioxide production by two authentic Marburg cultures, first under anaerobic (nitrogen), and then under aerobic conditions (air) is given in Fig. 2. The small initial amount of carbon dioxide given off under nitrogen may have been due to the presence of dissolved oxygen in the medium. The typical production of carbon dioxide under anaerobic conditions by a Ford culture is given for comparison. These results showed that the Marburg strains tested were strict aerobes which did not dissimilate glucose under anaerobic conditions on the media used. However, Knaysi and Gunsalus (3) found that by the addition of nitrate to the glucose medium some carbon dioxide was produced anaerobically.

Carbon balances are given in Table I for comparison of Marburg and Ford strains under aerobic conditions. Except for the fact that the Marburg cultures did not produce ethanol there was little difference.

Anaerobic Dissimilation of Glucose by Bacillus subtilis (Ford Type)

All the cultures were tested to find their rate of glucose dissimilation. Carbon balances were then determined on some of the faster fermenting strains. The product yields from three named cultures and nine isolates are given in Table II. The results are similar except for Strain 198. The best yield of 2,3-butanediol and glycerol accounts for 86% of the glucose and is somewhat better than that previously obtained. As the yield of 2,3-butanediol and glycerol decreases, the yield of lactic acid tends to increase. With Culture 198 lactic acid is the main product; 2,3-butanediol and acetoin account for only 8.7% of the glucose, while no glycerol was found. In spite of this marked difference in fermentative properties it was not possible on the basis of other criteria to segregate this culture from the *subtilis* group. Possibly a larger percentage of strains producing mainly lactic acid could be found if more cultures with a slower rate of fermentation were investigated.

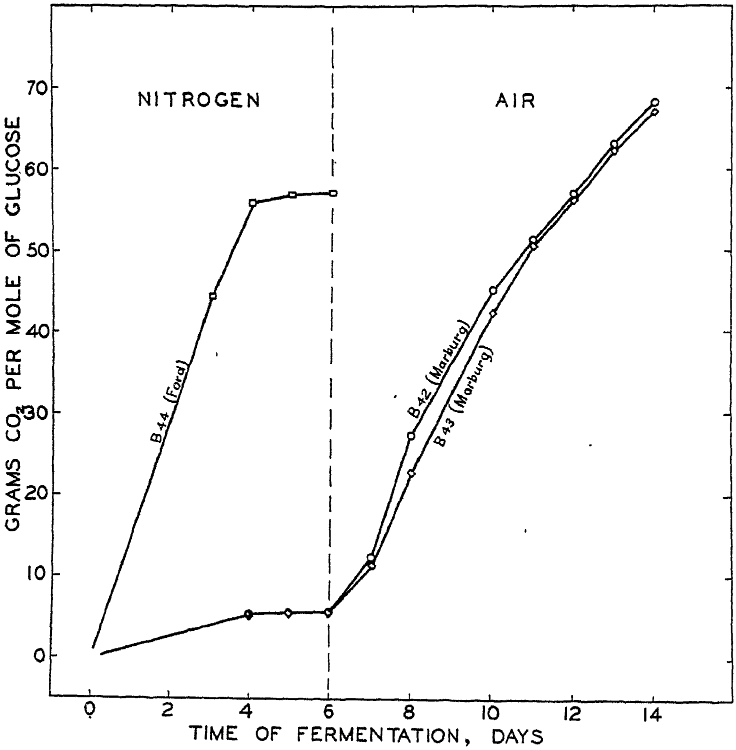

FIG. 2. *Rate of glucose dissimilation by Marburg and Ford types of Bacillus subtilis. Both types were grown anaerobically for six days and then the Marburg strains were grown aerobically for a further eight days.*

In order to assess the fermentation characteristics of a further group of cultures, analyses for the major products only were obtained for 18 isolates. The results are given in Table III. The product yields obtained from these cultures follow trends similar to those given in Table II. As much as 82% and as little as 8% of the glucose was converted to 2,3-butanediol and glycerol. Two cultures, like number 198, produced lactic acid as the main product.

Isolation and Identification of the Fermentation Products

Cultures 5, 7, 42, 43, 44, 106, 117, 138, 161, 198, 298, 299, and 304 were each grown in two litres of medium and the products isolated and identified by the melting point and the mixed melting point (with an authentic sample) of the

TABLE I

DISSIMILATION OF GLUCOSE UNDER AEROBIC CONDITIONS BY STRAINS OF *Bacillus subtilis*

Product	mM. product per 100 mM. glucose dissimilated		
	B42*	B43*	B2*
2,3-Butanediol	30.41	30.65	33.35
Acetoin	24.61	30.08	33.63
Glycerol	2.27	1.97	3.66
Ethanol	Nil	Nil	7.38
Formic acid	0.19	0.31	1.03
Acetic acid	4.23	3.64	4.89
n-Butyric acid	8.05	6.52	1.24
Lactic acid	1.76	1.25	1.77
Carbon assimilated	—	—	34.00
Carbon dioxide	285.0	284.0	207.58
Hydrogen	Nil	Nil	Nil
Time of fermentation, days	7	7	8
Glucose dissimilated, %	53.4	53.4	98.9
Carbon recovered, %	93.6	98.3	93.0

* *Named cultures previously described, B42 and B43, Marburg, B2, Ford strain.*

Conditions: Grown at 30° C. using 150 ml. medium in a 1000 ml. Erlenmeyer. Carbon-dioxide–free air was bubbled through at 12 to 14 ml. per min.

TABLE II

DISSIMILATION OF GLUCOSE UNDER ANAEROBIC CONDITIONS BY VARIOUS FORD TYPE STRAINS OF *Bacillus subtilis*

Product	Culture number											
	5*	7*	44*	200	161	299	298	304	107	117	138	198
	mM. product per 100 mM. of glucose dissimilated											
2,3-Butanediol	48.50	37.98	38.67	54.73	54.60	51.80	47.4	42.96	36.10	39.61	36.65	8.12
Acetoin	1.04	0.63	1.33	1.59	1.56	0.67	0.3	0.57	0.42	0.19	0	0.55
Glycerol	46.40	34.41	37.42	57.50	56.80	41.30	42.2	39.59	44.80	36.33	31.40	—
Ethanol	21.58	15.48	13.37	7.85	7.65	12.22	9.6	12.63	7.45	10.01	14.59	4.58
Formic acid	19.60	15.65	10.23	1.20	1.32	8.24	8.0	9.50	6.38	6.06	8.18	24.17
Acetic acid	0.56	1.32	1.64	—	0.16	—	—	—	—	—	—	6.99
n-Butyric acid	—	—	—	—	0.46	—	—	—	—	—	—	—
Lactic acid	24.81	54.70	47.50	23.13	17.61	38.50	44.6	54.10	62.20	59.80	73.45	137.10
Succinic acid	1.71	0.32	0.25	1.12	1.08	0.40	0.2	0.75	0.54	0.59	0.77	4.57
Malic acid	—	—	—	—	—	—	0.5	—	—	—	—	—
Carbon dioxide	112.9	85.7	93.1	114.9	117.8	102.2	97.1	88.8	77.6	87.1	72.5	4.43
Hydrogen	0	0	0	0	0.16	0.30	0.3	0	0.65	0.43	0	0
Fermentation time, days	5	6	6	8	11	9	6	11	9	11	7	11
Glucose fermented, %	99.2	99.2	99.2	99.5	99.7	99.6	99.6	99.5	90.4	99.7	99.8	52.2
Carbon recovered, %	99.5	93.2	92.0	100.0	98.0	97.8	96.4	97.1	95.7	94.0	93.7	86.4
O/R Index	1.00	1.03	1.07	0.96	0.99	0.96	1.00	0.97	0.96	1.03	0.90	1.08

* *Named cultures described previously.*

Conditions: Grown at 34° C. using 150 ml. medium in a 1000 ml. Erlenmeyer. Oxygen-free nitrogen was bubbled through at 12 to 14 ml. per min.

TABLE III

ANAEROBIC DISSIMILATION OF GLUCOSE BY VARIOUS OTHER FORD STRAINS OF *Bacillus subtilis*

Culture No.	% Glucose dissimilated	mM. product per 100 mM. glucose fermented				% of dissimilated glucose accounted for*
		2,3-Butanediol	Glycerol	Ethanol	Lactic acid	
158	98.4	55.20	54.40	13.00	16.51	97.2
205	98.8	50.95	51.80	14.50	25.61	96.9
167	99.0	50.45	51.80	12.82	32.10	98.7
165	98.4	47.60	52.50	10.18	20.65	89.3
166	98.7	50.90	48.20	19.60	32.40	101.0
164	99.3	46.90	52.20	6.71	40.00	93.4
339	96.0	55.70	42.60	20.90	17.53	96.2
345	94.5	54.60	39.40	22.42	21.45	95.7
350	97.5	56.15	34.60	21.82	28.18	98.4
211	99.0	49.40	36.41	17.52	35.09	93.9
136	77.4	40.00	33.22	13.45	49.80	88.2
108	89.3	42.55	30.85	16.81	40.95	86.9
343	98.2	38.61	32.20	19.75	41.60	85.4
346 (a)	98.8	38.40	32.15	16.92	53.51	89.7
137	99.1	47.00	21.70	21.55	47.20	92.2
172	73.6	38.10	22.20	20.80	53.38	86.3
163	53.8	7.80	Tr	4.74	134.50	77.4
210	53.5	8.01	—	3.30	142.20	80.8

* *The calculation was made by assuming that from one mole of glucose is produced one mole of 2,3-butanediol, or two moles of glycerol, ethanol, or lactic acid.*

Time of fermentation was 11 days at 37° C. under anaerobic conditions (oxygen-free nitrogen), using 150 ml. medium in a 1000 ml. Erlenmeyer.

TABLE IV

A COMPARISON OF THE PROPERTIES OF 2,3-BUTANEDIOL AND LACTIC ACID PRODUCED BY VARIOUS *Bacillus subtilis* CULTURES

Culture No.	2,3-Butanediol			Lactic acid	
	$[\alpha]_D^{25}$	Refractive index at 25° C.	Boiling point, ° C.	*% dextro*	*% levo*
5	−4.86°	1.4311	177–180	87.2	12.8
44	−4.17°	1.4338	177–180	78.6	21.4
7	−3.86°	1.4332	177–180	89.2	10.8
161	−3.86°	1.4340	177–180	92.8	7.2
299	−3.89°	1.4333	177–180	93.1	6.9
298	−4.06°	1.4343	177–180	91.6	8.4
304	−4.39°	1.4345	129–134*	91.6	8.4
117	−4.63°	1.4330	177–181	95.6	4.4
138	−4.23°	1.4331	177–180	53.7	46.3
198	—	No data	—	94.6	5.4
106	−4.36°	1.4345	177–184	95.1	4.9

**At 10 cm. pressure; the others are at 76 cm.*

crystalline derivative. The Marburg cultures, numbers 42 and 43, fermented only half the glucose, and, as they produced about equal amounts of 2,3-butanediol and acetoin, it was not possible to recover sufficient of the 2,3-butanediol to determine its properties. The acetoin in this case was identified. No ethanol was obtained from these Marburg cultures, as the carbon balance data show.

Table IV gives the properties of the 2,3-butanediol and lactic acid produced by the Ford type cultures. The rotation and other properties of the 2,3-butanediol vary little among this selection of strains. However, the relative amounts of the lactic acid isomers produced vary from a slight excess of *dextro-* to nearly all *dextro*-lactic acid.

Discussion

Thirty Ford type cultures have been assessed in detail. Extreme variations in the yield of the various products have been obtained. With some strains 86% of the glucose is accounted for by the following equation:

$$3C_6H_{12}O_6 \longrightarrow 2CH_3.CHOH.CHOH.CH_3 + 2CH_2OH.CHOH.CH_2OH + 4CO_2\,.$$

In the previous study (7) the yield of glycerol was somewhat lower than that theoretically possible, based on the yield of 2,3-butanediol. However, a number of cultures have now been obtained that give approximately equal molar yields of these two products. These experiments have all been carried out under the conditions previously found to give the best yield of glycerol (7). It is hoped that a further investigation of environmental conditions with individual cultures may give faster fermentation rates and possibly an increased yield of the desired products. In a previous paper (7) it was concluded that the high yields of lactic acid reported by various investigators as being produced by *Bacillus subtilis* were in part due to fermentation conditions. However, the results obtained with certain strains indicate that the culture used is also important.

The designation by the Second International Congress for Microbiology of the Marburg strain as the type strain of the *Bacillus subtilis* species has not solved the taxonomic difficulties. The investigations of Lamanna (4), Knaysi and Gunsalus (3), and Gibson (1) have shown that the strains described by Ford (5) as *subtilis* differ from the type strain sufficiently to be considered as a distinct species; in fact Gibson has separated these Ford strains and named them *Bacillus licheniformis* (Weigmann) Gibson (1). In addition to other criteria the faster rate of carbon dioxide production from glucose by the Ford type cultures has been noted. Our results show this distinction more definitely, in that under anaerobic conditions there is no fermentation by the Marburg strains and a good rate of fermentation by the Ford strains. It was possible to separate the two types on this basis alone. It is significant that in the aerobic dissimilation of glucose, although the products produced by the two types are similar, the Marburg cultures do not give ethanol. These results are a further indication that the Ford strains of *Bacillus subtilis* are distinctive enough from the type strain (Marburg) to be given separate species rank.

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PRODUCTION AND PROPERTIES OF 2,3-BUTANEDIOL

XVIII. DISSIMILATION OF GLUCOSE BY *SERRATIA MARCESCENS*[1]

By A. C. Neish[2], A. C. Blackwood[3], F. M. Robertson[2],
and G. A. Ledingham[4]

Abstract

Four strains of *Serratia marcescens* were found to dissimilate glucose under anaerobic conditions, producing 2,3-butanediol according to the equation: $C_6H_{12}O_6 \longrightarrow CH_3 . CHOH . CHOH . CH_3 + HCOOH + CO_2$. Under aerobic conditions little formic acid was produced and the reaction became $C_6H_{12}O_6 + \frac{1}{2}O_2 \longrightarrow CH_3 . CHOH . CHOH . CH_3 + H_2O + 2CO_2$. These reactions accounted for 40 to 60% of the glucose. The remainder was fermented to lactic acid (5 to 25%), ethanol (10 to 20%) and glycerol (1 to 4%). The lactic acid produced was 95 to 97% of the *levo*-isomer; the 2,3-butanediol was a *meso-dextro* mixture containing about 2% of the *dextro*-isomer.

Introduction

Pederson and Breed (7) made the first study of the products formed on dissimilation of glucose by *Serratia marcescens.* The organisms were grown on a 1.0% peptone broth containing 3% glucose and buffered with calcium carbonate. The products obtained with a typical strain were lactic acid (40%), carbon dioxide (28%), acetoin and 2,3-butanediol (18%), acetic acid (5.8%), ethanol (4.7%), and formic acid (0.2%). Some hydrogen and succinic acid were also formed, the molecular ratio of carbon dioxide to hydrogen being about 10 : 1. The lactic acid was shown to be the *levo*-isomer but the configuration of the 2,3-butanediol was not determined. Sigurdsson and Wood (8) fermented glucose solutions, containing large amounts of trimethylamine oxide, with heavily buffered, washed-cell suspensions of *S. marcescens.* The yield of lactic acid varied with the pH but was 40 to 77% for the two strains used. The other products were acetic acid, formic acid, ethanol, carbon dioxide, and acetoin. No appreciable quantities of 2,3-butanediol were reported. In some experiments more than 20% of the glucose used was unaccounted for.

Organisms that produce 2,3-butanediol, but not hydrogen, are interesting because they may give good yields of glycerol under anaerobic conditions (3, 6). Since strictly anaerobic conditions were not used by the previous workers, it was considered worth while to investigate the glucose catabolism of several strains of *S. marcescens* that were known to yield little or no hydrogen. The

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[2] *Biochemist.*

[3] *Bacteriologist.*

[4] *Mycologist.*

dissimilation of glucose was studied using four strains under both anaerobic and aerobic conditions and on a synthetic medium as well as on one containing yeast extract.

Experimental and Results

Organisms and Media

The four strains of *Serratia marcescens* used were:

S1 and S3—isolated in this laboratory and classified as *Serratia marcescens*, following the key in Bergey's Manual (2).

S2—received from the Department of National Health and Welfare, Ottawa, Canada.

S9—American Type Culture Collection Strain Number 264.

The two media used were:

(*a*) *Yeast-extract medium*—glucose (5%), yeast extract (0.5%), potassium dihydrogen phosphate (0.05%), potassium monohydrogen phosphate (0.05%), and magnesium sulphate (0.02%).

(*b*) *Synthetic medium*—composition the same as the above except that the yeast extract was replaced by 0.25% ammonium chloride.

These were both buffered with calcium carbonate (2%), which was sterilized separately and added just before use. The inoculum was incubated overnight at 37° C. in 10 ml. of a medium containing glucose (1%) and yeast extract (0.5%). This was used to inoculate 150 ml. of either of the above media.

Dissimilation of Glucose

The products of glucose dissimilation were determined under both aerobic and anaerobic conditions, using the methods previously described (3, 6).

The chief products obtained, in the absence of oxygen, were 2,3-butanediol, formic acid, ethanol, lactic acid, and carbon dioxide (Table I). The four strains gave similar results although S9 yielded considerably more succinic and lactic acids and less of the other products. All gave small amounts of acetoin and glycerol but little or no hydrogen.

The introduction of air greatly depressed formic acid production although the amounts of 2,3-butanediol, acetoin, and carbon dioxide formed were greater (Table II). Acetic acid, which may be formed by oxidation of the ethanol, appeared as a product. The fermentations were more rapid under aerobic conditions both on the synthetic medium and on that containing yeast extract. The yeast extract enabled all the strains to dissimilate nearly twice as much glucose during the first day but, in spite of this, some fermentations were completed first on the synthetic medium. The presence of yeast extract favours the production of lactic acid and depresses the formation of formic acid. These are the only effects, of addition of yeast extract, common to all strains.

TABLE I

ANAEROBIC DISSIMILATION OF GLUCOSE BY *Serratia marcescens*

Products	mM. of products per 100 mM. of glucose dissimilated			
	Strain S1	Strain S2	Strain S3	Strain S9
2,3-Butanediol	57.90	55.20	51.45	42.45
Acetoin	0.25	0.50	0.81	1.14
Glycerol	6.14	4.18	4.54	5.63
Ethanol	40.85	41.30	42.24	25.90
Lactic acid	15.70	26.50	33.09	54.15
Formic acid	48.50	44.00	39.80	27.60
Acetic acid	Nil	Nil	Nil	Nil
Succinic acid	2.98	3.34	3.41	18.80
Carbon dioxide	103.8	102.5	106.1	78.2
Hydrogen	Nil	Nil	0.52	0.27
Fermentation time, days	17	12	9	7
Glucose dissimilated, %	93.2	88.5	99.5	99.9
Carbon accounted for, %	91.4	93.0	94.6	97.5
O/R index	0.99	1.03	1.04	1.01

The bacteria were grown in the yeast-extract medium (150 ml. in a one litre Erlenmeyer flask) at 35° C. The medium was buffered with excess calcium carbonate (2%), and anaerobic conditions were maintained by continuous passage of oxygen-free nitrogen through the solution.

TABLE II

AEROBIC DISSIMILATION OF GLUCOSE BY *Serratia marcescens*

Products	mM. of products per 100 mM. of glucose dissimilated							
	Strain S1		Strain S2		Strain S3		Strain S9	
	Yeast-extract medium	Synthetic medium	Yeast-extract medium	Synthetic medium	Yeast-extract medium	Synthetic medium	Yeast-extract medium	Synthetic medium
2,3-Butanediol	62.48	58.45	56.30	59.60	55.40	52.55	41.10	48.90
Acetoin	3.31	7.45	7.51	7.52	6.56	7.92	7.10	7.59
Glycerol	1.39	1.73	1.93	1.08	1.99	1.18	1.11	Nil
Ethanol	38.30	29.80	33.25	25.30	29.65	32.80	36.10	31.10
Lactic acid	9.89	6.05	9.20	4.90	22.70	11.70	13.30	7.73
Formic acid	3.64	4.56	1.05	3.91	1.61	3.13	2.05	3.14
Acetic acid	3.48	7.78	8.40	8.40	5.52	4.94	8.19	5.55
Succinic acid	7.71	4.67	7.40	5.12	6.12	8.59	18.10	17.99
Carbon dioxide	177.8	164.8	163.3	151.5	154.5	154.0	159.0	157.2
Hydrogen	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil
Fermentation time, days	5	3	5	5	3	4	5	5
Glucose dissimilated, %	99.9	99.9	99.8	100.0	99.6	100.0	100.0	100.0
Carbon accounted for, %	98.8	92.0	94.4	90.0	95.4	91.4	93.1	92.4

In all experiments 150 ml. of medium was used in a one litre Erlenmeyer flask; a current of carbon-dioxide-free air was bubbled through continuously at the rate of 80 to 90 ml. per hr. The media were buffered with excess calcium carbonate (2%) and maintained at a temperature of 35° C.

Succinic acid is produced by all strains, particularly S9, which yields 12 gm. of succinic acid for every 100 gm. of glucose fermented. Its production is not influenced by aeration or by adding yeast extract to the medium.

The major products of two of these strains were isolated and identified as crystalline derivatives using the methods previously described (3, 6). The 2,3-butanediol is chiefly the *meso*-isomer but a small amount of the *dextro*-isomer is present; the lactic acid is predominantly *levo* (see Table III).

TABLE III

NATURE OF THE 2,3-BUTANEDIOL AND LACTIC ACID PRODUCED BY *Serratia marcescens*

——	Strain S1	Strain S3
Boiling point of 2,3-butanediol, ° C.	181 to 184	181 to 184
Refractive index of 2,3-butanediol, 25° C.	1.4354	1.4350
$[\alpha]_D^{25}$ of 2,3-butanediol	+0.07	+0.35
Lactic acid; per cent as *levo*-isomer	95	93
Lactic acid; per cent as *dextro*-isomer	5	7

The bacteria were grown in the yeast-extract medium buffered with calcium carbonate (2%), at 35° C. under anaerobic conditions.

Discussion

The anaerobic dissimilation of glucose by *Serratia marcescens* has not been studied previously. Pederson and Breed's (7) studies on mildly aerobic glucose dissimilation by this species agree in a general way with our results, except that we obtained little or no hydrogen. The other differences may be due to differences in the media, between strains, or in the degree of aeration.

Succinic acid is produced by all strains, particularly S9. Since it is produced just as readily on a medium containing glucose as the sole source of carbon as it is on a medium containing added yeast extract, it is regarded as a product originating from glucose rather than from proteins.

Bacteria are able to convert glucose to 2,3-butanediol by four different fermentations. The best known of these is described by the equation:

$$C_6H_{12}O_6 \longrightarrow CH_3 . CHOH . CHOH . CH_3 + H_2 + 2CO_2 .$$

This reaction is catalyzed by *Aerobacter aerogenes* (4, 5) *Aerobacillus polymyxa* (1) and *Aeromonas hydrophila* (9), and has been known for almost 40 years. Recently it has been found (3, 6) that the Ford type of *Bacillus subtilis* produces 2,3-butanediol according to the following equation:

$$3C_6H_{12}O_6 \longrightarrow 2CH_3 . CHOH . CHOH . CH_3 + 2CH_2OH . CHOH . CH_2OH + 4CO_2 .$$

The other two fermentations are carried out with *Serratia marcescens:*

$$C_6H_{12}O_6 \longrightarrow CH_3 . CHOH . CHOH . CH_3 + HCOOH + CO_2$$

$$C_6H_{12}O_6 + \tfrac{1}{2} O_2 \longrightarrow CH_3 . CHOH . CHOH . CH_3 + H_2O + 2CO_2 .$$

The first of these describes the fermentation of glucose under anaerobic conditions, the second its dissimilation under aerobic conditions.

All these bacteria catalyze parallel reactions, particularly the lactic acid fermentation, or the ethanol fermentation. In addition, *S. marcescens* produces some of its 2,3-butanediol by the diol–glycerol fermentation, and *B. subtilis* a little by the diol–formic-acid fermentation. The closest approach to a homofermentative organism, as far as these equations are concerned, is found with certain strains of *B. subtilis* which dissimilated 86% of the glucose according to the above equation for the 2,3-butanediol–glycerol fermentation, and strains of *A. aerogenes* which give 90% of the 2,3-butanediol–hydrogen fermentation.

The equations given above do not explain the mechanism of the formation of 2,3-butanediol from sugars but merely state the over-all yields of products that can be expected. It is possible that organisms will be found that dissimilate practically all the glucose according to one or other of these equations.

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PRODUCTION AND PROPERTIES OF 2,3-BUTANEDIOL

XIX. CYCLIC ACETALS AND KETALS DERIVED FROM *LEVO*-2,3-BUTANEDIOL[1]

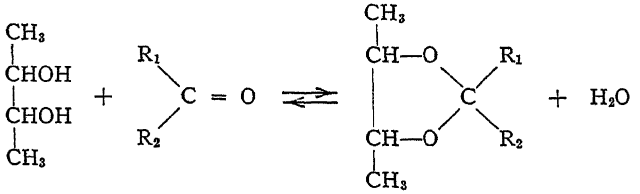
BY A. C. NEISH[2] AND F. J. MACDONALD[2]

Abstract

Optically active 4,5-dimethyl-1,3-dioxacyclopentane derivatives can be easily obtained by condensing *levo*-2,3-butanediol with aldehydes or ketones in the presence of small amounts of strong acids at ordinary temperatures. Condensations were effected with formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, isobutyraldehyde, 2-ethylbutyraldehyde, 2-ethylhexaldehyde, benzaldehyde, furfural, acrolein, acetone, methyl ethyl ketone, methyl isobutyl ketone, methyl amyl ketone, diethyl ketone, acetophenone, cyclohexanone, acetoin, and diacetyl. The expected products were obtained, two compounds being formed from diacetyl since one or both carbonyl groups may react. Two compounds were obtained from formaldehyde also; in addition to the expected product (*levo*-4,5-dimethyl-1,3-dioxacyclopentane), 15 to 20% of *levo*-6,7-dimethyl-1,3,5-trioxacycloheptane was obtained.

Backer (1) observed that 2,3-butanediol condensed readily with formaldehyde, acetaldehyde, acetone, methyl ethyl ketone, cyclohexanone, benzaldehyde, and ethyl cyclohexanone-4-1-carboxylate to give 4,5-dimethyl-1,3-dioxacyclopentane derivatives. The sample of diol he used was prepared by fermentation and was probably the *meso-dextro* mixture produced by *Aerobacter aerogenes*, which is 90 to 95% of the *meso*-isomer. If this were the case Backer's compounds were *meso*-4,5-dimethyl-1,3-dioxacyclopentane derivatives. The present work is concerned with the optically active *levo*-4,5-dimethyl-1,3-dioxacyclopentane derivatives prepared from the pure *levo*-2,3-butanediol produced by *Aerobacillus polymyxa* (2).

The general reaction is:



A series of aldehydes and ketones were found to give the expected reaction products. The compounds prepared are listed in Table I, together with their physical properties. The molar refractions agree well with the calculated values. This, in conjunction with the analytical data given in the experimental section, is taken as proof of their structure. In general the *levo*-isomers have a lower boiling point, refractive index and density than the

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[2] *Biochemist.*

TABLE I

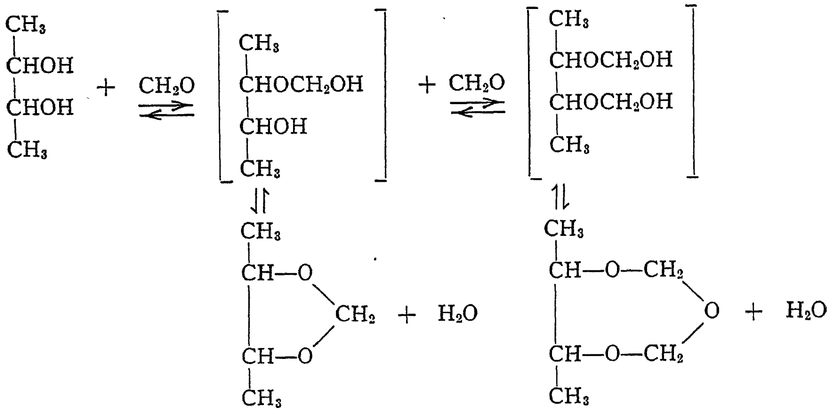
PHYSICAL PROPERTIES OF CYCLIC ACETALS AND KETALS DERIVED FROM *levo*-2,3-BUTANEDIOL

Compound	Boiling point, °C. at 760 mm.	Refractive index at 25° C.	Density d_4^{25}	Optical rotation $[\alpha]_D^{25}$ (degrees)	Molar refraction	
					Calculated	Found
levo-4,5-Dimethyl-1,3-dioxacyclopentane	97	1.3960	0.9346	− 24.9	26.38	26.25
levo-2,4,5-Trimethyl-1,3-dioxacyclopentane	103	1.3924	0.8914	− 21.8	30.98	31.02
levo-4,5-Dimethyl-2-ethyl-1,3-dioxacyclopentane	127	1.4014	0.8868	− 14.0	35.59	35.58
levo-4,5-Dimethyl-2-propyl-1,3-dioxacyclopentane	150	1.4075	0.8824	− 14.2	40.19	40.17
levo-4,5-Dimethyl-2-isopropyl-1,3-dioxacyclopentane	140	1.4062	0.8822	− 16.5	40.19	40.16
levo-4,5-Dimethyl-2-(2-ethylbutyl)-1,3-dioxacyclopentane	180	1.4202	0.8842	− 16.9	49.42	49.56
levo-4,5-Dimethyl-2-(2-ethylhexyl)-1,3-dioxacyclopentane	215	1.4275	0.8874	− 14.9	58.62	58.69
levo-4,5-Dimethyl-2-phenyl-1,3-dioxacyclopentane	230	1.4982	1.0274	− 28.1	50.71	50.76
levo-4,5-Dimethyl-2-vinyl-1,3-dioxacyclopentane	132	1.4173	0.9155	− 24.3	35.19	35.21
levo-4,5-Dimethyl-2-furyl-1,3-dioxacyclopentane	206	1.4645	1.0770	− 26.6	43.58	43.12
levo-2,2,4,5-Tetramethyl-1,3-dioxacyclopentane	110	1.3914	0.8669	− 22.1	35.59	35.71
levo-2,4,5-Trimethyl-2-ethyl-1,3-dioxacyclopentane	134	1.4025	0.8749	− 18.8	40.19	40.18
levo-2,4,5-Trimethyl-2-isobutyl-1,3-dioxacyclopentane	166	1.4110	0.8621	− 14.0	49.94	49.61
levo-2,4,5-Trimethyl-2-amyl-1,3-dioxacyclopentane	192	1.4178	0.8652	− 17.0	54.00	54.09
levo-2,4,5-Trimethyl-2-phenyl-1,3-dioxacyclopentane	219	1.4868	0.9989	− 40.7	55.31	55.12
levo-2,2-Diethyl-4,5-dimethyl-1,3-dioxacyclopentane	155	1.4109	0.8808	− 12.6	44.79	44.61
levo-2,4,5-Trimethyl-2-(*dl*-α-hydroxy ethyl)-1,3-dioxacyclopentane	181	1.4273	0.9901	− 21.0	41.71	41.56
dextro-2,4,5-Trimethyl-2-aceto-1,3-dioxacyclopentane	177	1.4170	0.9857	+ 13.15	40.37	40.36
levo-Bis-2,2′-(2,4,5-trimethyl-1,3-dioxacyclopentane)	222	1.4450	1.0281	−101.5	59.87	59.61
levo-6,7-Dimethyl-1,3,5-trioxacycloheptane	152	1.4299	1.0336	− 61.2	32.67	33.01
levo-3,4-Dimethyl-2,5-dioxa-1-spirodecane	190	1.4438	0.9546	− 7.0	47.29	47.35

analogous compounds prepared by Backer (1). For example, *levo*-2,2,4,5-tetramethyl-1,3-dioxacyclopentane boils at 110° C. while Backer's analog has a boiling point of 117.5° to 118.5° C.

Two compounds were obtained on condensing formaldehyde with *levo*-2,3-butanediol. If the formaldehyde is bubbled into a mixture of the diol and hydrochloric acid, and the temperature allowed to rise to the point of reflux, the normal reaction product, *levo*-4,5-dimethyl-1,3-dioxacyclopentane (I), is the only one obtained. If, however, excess formaldehyde is bubbled into the *levo*-2,3-butanediol containing a small amount of hydrochloric acid and the mixture is kept cool until addition of the formaldehyde is completed, then *levo*-6,7-dimethyl-1,3,5-trioxacycloheptane (II) may be obtained in yields up to 20% of the theoretical.

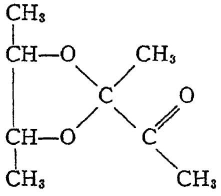
The formation of these compounds may be visualized as follows:



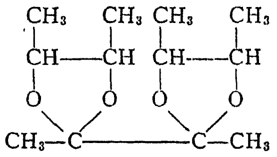
I II

The intermediate hemiacetals were not isolated in the pure state but it was possible to demonstrate that intermediates with high boiling points were present in the reaction mixture.

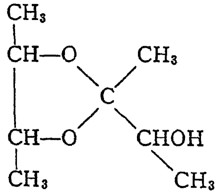
Two compounds were obtained from diacetyl as expected. These were *dextro*-2,4,5-trimethyl-2-aceto-1,3-dioxacyclopentane (III) and *levo*-bis-2,2'-(2,4,5-trimethyl-1,3-dioxacyclopentane) (IV).



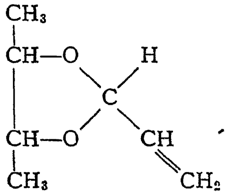
III



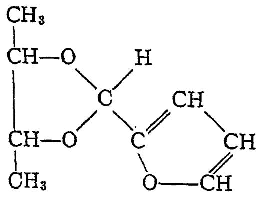
IV



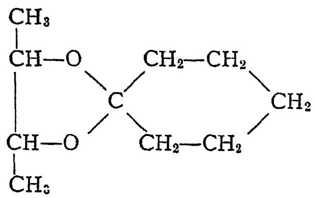
V



VI



VII



VIII

Acetoin condenses readily to give the hydroxyketal V, which is the only compound of those prepared that is miscible with water; it is also miscible with Skelly-solve. Acrolein condenses smoothly to give the vinylacetal VI in yields about 60% of the theoretical. Furfural reacts to give the furylacetal VII and cyclohexanone to give *levo*-3,4-dimethyl-2,5-dioxa-1-spirodecane (VIII.) The *meso*-isomer of the latter compound was prepared by Backer (1).

These compounds are resistant to alkaline hydrolysis but are readily hydrolysed by dilute acids to the compounds from which they were made. Like ethers they form peroxides when exposed to air, particularly in the light.

l-2,3-Butanediol reacts with ketones very readily; it reacts more rapidly than 1,3-butanediol, 1,3-propanediol, 1,2-propanediol, or ethanediol.

Experimental

General

The reactions were usually carried out by mixing *levo*-2,3-butanediol and the carbonyl compound in equimolar amounts and adding 1 to 5 ml. of concentrated sulphuric or hydrochloric acid per mole. This mixture was shaken or stirred and the temperature allowed to rise to 40° to 50° C. In most cases the products were insoluble in water and a two phase system formed. After the reaction was judged to be complete, the water layer was separated, and discarded, the acetal layer was washed with saturated sodium bicarbonate solution, filtered through anhydrous sodium sulphate and fractionally distilled through a column filled with glass helices or Stedman packing. The product was refractionated, and measurements made of its density, refractive index, optical rotation, and boiling point. A sample was analysed as a check on its identity. This was done by hydrolysing an accurately weighed amount of the compound with normal hydrochloric or sulphuric acid in a pressure bottle (one hour at 100° C.) and determining the 2,3-butanediol in the hydrolysate. The diol was determined by treating a suitable aliquot with 5 ml. of 0.1 *M* sodium periodate for one hour at room temperature; the periodate reduced was then determined iodometrically by the procedure of Rappaport, Reifer, and Weinmann (4). This procedure worked well on all the compounds except those derived from formaldehyde and diacetyl. These were difficult to hydrolyse quantitatively, particularly the latter. They were analysed by combustion.

Because of the reversible nature of the condensation the yields obtained are minimum values. There is no evidence of side reactions; the yields are not quantitative because the reaction reaches an equilibrium. It is not always certain that enough time was allowed for the equilibrium value to be reached.

levo-4,5-Dimethyl-1,3-dioxacyclopentane and levo-6,7-Dimethyl-1,3,5-trioxacycloheptane

Five moles of *levo*-2,3-butanediol and 5 ml. of concentrated hydrochloric acid were mixed in a two litre, three-necked flask equipped with a stirrer and cooled in a water-bath. Paraformaldehyde (8 moles) was heated in a separate flask and the gaseous formaldehyde thus obtained bubbled into the acid–diol mixture, which warmed spontaneously to 50° to 60° C. After addition of the formaldehyde was complete (1.5 hr.) 20 ml. of hydrochloric acid was added and the solution warmed gently until it became diphasic. The top layer was separated, washed with saturated sodium bicarbonate solution, filtered through anhydrous sodium sulphate, and distilled through a 2 ft. column packed with glass helices. The products obtained were (*a*) a diphasic azeotrope boiling at 81° to 82° C.; (*b*) a liquid boiling at 97° C., and (*c*) a liquid boiling at 152° C.

The azeotrope had a top layer, the volume of which was 7.0 times that of the bottom. This top layer was separated and on distillation gave some more azeotrope, b.p. 81° to 82° C., but chiefly the liquid, b.p. 97° C. This compound is *levo*-4,5-dimethyl-1,3-dioxacyclopentane and the azeotrope is that formed with water. Its physical properties are given in Table I. It is a colourless liquid with an agreeable odour. Yield, 63% of theory, based on the diol. Found: C, 58.9, 58.9; H, 9.98, 9.80%. Cal. for $C_5H_{10}O_2$: C, 58.8; H, 9.87%. The *meso*-isomer of this compound (b.p. 102° to 103° C.) was prepared by Backer (1).

The liquid with b.p. 152° C. was redistilled and analysed. Found: C, 54.5, 54.5; H, 9.18, 9.12%; halogen, nil. Calc. for $C_6H_{12}O_3$: C, 54.5; H, 9.15%. It is a colourless liquid, immiscible with water, having an odour similar to that of the formal. On hydrolysis with acid it gives two moles of formaldehyde per mole of 2,3-butanediol. The only logical structure to assign to this compound on the basis of these facts is *levo*-6,7-dimethyl-1,3,5-trioxacycloheptane. Its physical properties are given in Table I. The yield was 14% of theory, based on the diol.

Backer (1) did not obtain a compound analogous to this. If the condensation is allowed to proceed rapidly by adding all of the acid at the start and letting the mixture warm up, it is not obtained in any appreciable amounts. Its yield can be increased to about 20% by carrying out the condensation at lower temperatures. An attempt was made to isolate intermediate hemiacetals by neutralizing the solution with sodium hydroxide after the formaldehyde (8 moles) had been bubbled into the mixture of diol (5 moles) and hydrochloric acid (5 ml.). The monophasic reaction mixture was then distilled, to give the formal–water azeotrope (0.6 moles), formaldehyde, unchanged *levo*-2,3-butanediol (2 moles) and 230 ml. of a viscous, colourless liquid boiling over the range 103° to 225° C. (10 mm.). This fraction had an observed optical rotation (*D* line) of − 59.6° per decimetre. After it had stood overnight at room temperature it was redistilled and 113 ml. of the formal–water azeotrope and 85 ml. of *levo*-2,3-butanediol obtained. Apparently there are high-boiling unstable intermediates formed, but their constitution is uncertain since they could not be obtained in a pure condition owing to their instability.

levo-2,4,5-Trimethyl-1,3-dioxacyclopentane

Paraldehyde (6 moles) and *levo*-2,3-butanediol (6 moles) were mixed and treated with concentrated sulphuric acid (15 gm.). After reaction had continued for one hour at 40° to 50° C. the top layer was separated and the bottom layer extracted with ether. The extract was combined with the acetal layer, washed with sodium bicarbonate solution, filtered through anhydrous sodium sulphate and distilled through a Stedman column. The acetal was obtained as a colourless liquid, b.p. 103° C., with a very pleasant odour (yield, 34% of theory). It was refractionated and its physical properties determined (see Table I). Equivalent weight (periodate reduction): calc., 58.1; found: 58.0. Backer (1) prepared the *meso*-isomer of this compound (b.p. 108° to 109° C.).

An attempt was made to prepare a 1,3,5-trioxacycloheptane derivative by mixing acetaldehyde (11.4 moles) with *levo*-2,3-butanediol (3.8 moles) and adding a trace of hydrochloric acid. The acetal and paraldehyde were the only products obtained.

levo-4,5-Dimethyl-2-ethyl-1,3-dioxacyclopentane

Propionaldehyde (5 moles) and *levo*-2,3-butanediol (5 moles) were mixed and treated with hydrochloric acid (5 ml.) added with shaking (15 min.). The mixture was kept cooled below 50° C. The top layer was then separated, treated as usual, and fractionated through a Stedman column. The product is a colourless liquid, b.p. 126° to 127° C., with an odour similar to that of the acetal (yield, 86% of theory). It was refractionated through a column packed with glass helices and its physical properties determined (Table I). Equivalent weight (periodate reduction): calc., 65.1; found, 65.6.

levo-4,5-Dimethyl-2-propyl-1,3-dioxacyclopentane

This was prepared from *n*-butyraldehyde and *levo*-2,3-butanediol by the general procedure using hydrochloric acid. The product is a liquid, b.p. 149° to 150° C. (yield, 75% of theory). It was refractionated and its physical properties determined (Table I). Equivalent weight (periodate reduction): calc., 72.1; found, 72.0.

levo-4,5-Dimethyl-2-isopropyl-1,3-dioxacyclopentane

This was prepared from isobutyraldehyde and *levo*-2,3-butanediol by the general procedure using hydrochloric acid. The product is a colourless liquid, b.p. 139° to 140° C. (yield, 58% of theory). It was refractionated and its physical properties determined (Table I). Equivalent weight (periodate reduction): calc., 72.1; found, 71.6.

levo-4,5-Dimethyl-2-(2-ethylbutyl)-1,3-dioxacyclopentane

This was prepared from 2-ethylbutyraldehyde and *levo*-2,3-butanediol by the general procedure using hydrochloric acid. This acetal is a colourless liquid, b.p. 124° to 125° C. (134 mm.); yield, 77% of theory. It was refractionated to give a liquid, b.p. 135° C. (200 mm.). Its physical properties are shown in Table I. Equivalent weight (periodate reduction): calc., 86.1; found, 86.5.

levo-4,5-Dimethyl-2-(2-ethylhexyl)-1,3-dioxacyclopentane

This was prepared from 2-ethylhexaldehyde and *levo*-2,3-butanediol, by the general procedure, using hydrochloric acid. It is a colourless liquid, b.p. 147° to 148° C. (100 mm.); yield, 66% of theory. It was refractionated and its physical properties determined (Table I). It was necessary to use some methanol to bring it into solution for determination of its equivalent weight (periodate reduction): calc., 100.2; found, 100.7.

levo-4,5-Dimethyl-2-phenyl-1,3-dioxacyclopentane

This was prepared from benzaldehyde and *levo*-2,3-butanediol, by the general procedure, using hydrochloric acid. An emulsion formed which was treated with solid sodium bicarbonate and enough anhydrous sodium sulphate to remove the water. The filtrate was fractionated to give a colourless liquid, b.p. 153° to 154° C. (75 mm.); yield, 75% of theory. It was refractionated and its physical properties determined (Table I). Equivalent weight (periodate reduction): calc., 89.1; found, 89.8. The *meso*-isomer of this compound was prepared by Backer (1).

levo-4,5-Dimethyl-2-vinyl-1,3-dioxacyclopentane

This was prepared from freshly distilled acrolein (0.8 moles) and *levo*-2,3-butanediol (0.8 moles) by treating with hydrochloric acid (1 ml.) and shaking for 15 min. The top layer was purified and distilled as usual. The acetal was a colourless liquid boiling at 131° to 132° C. (yield, 60% of theory). It was refractionated and its physical properties determined (Table I). Equivalent weight (periodate reduction): calc. 64.1; found, 63.9. About 0.2 mole of acrolein was recovered unchanged. The yield in this reaction is high compared to that in the reaction between ethanol and acrolein.

levo-4,5-Dimethyl-2-furyl-1,3-dioxacyclopentane

Furfural and *levo*-2,3-butanediol were mixed and treated with hydrochloric acid. It is important not to use sulphuric acid, which causes tar formation. After reaction had continued for two hours the lower layer (acetal) was separated and the top layer extracted with ether, the extract being added to the acetal layer. After washing with sodium bisulphite and sodium bicarbonate solutions it was dried with sodium sulphate and distilled through the Stedman column. This acetal is a colourless liquid, b.p. 140° C. (100 mm.); yield, 50% of theory. Its odour is something like that of furfural. It was refractionated; its physical properties are given in Table I. Equivalent weight (periodate reduction): calc., 84.1; found, 84.1.

levo-2,2,4,5-Tetramethyl-1,3-dioxacyclopentane

This was prepared from acetone and *levo*-2,3-butanediol, using 3 ml. of hydrochloric acid per mole of diol. The reaction was run 14 hr. with stirring. This is longer than is necessary. The top layer was treated as usual and distilled through a column filled with glass helices. This ketal is a liquid, b.p. 110° C., with a camphor-like odour (yield, 52% of theory). Equivalent weight (periodate reduction): calc., 65.1; found, 65.0. Backer prepared the *meso*-isomer of this compound, b.p. 118° C. The *levo*-isomer gives a diphasic azeotrope with water, b.p. 86° C., the volume of the ketal layer being 6.7 times that of the water layer.

levo-2,4,5-Trimethyl-2-ethyl-1,3-dioxacyclopentane

This was prepared from methyl ethyl ketone (5 moles) and *levo*-2,3-butanediol, using 25 ml. of hydrochloric acid. The mixture was stirred 2½ hr. and the product worked up as usual. The ketal was obtained as a colourless liquid, b.p. 133° to 134° C., with an odour very much like that of camphor (yield, 60% of theory). It was refractionated through a column packed with glass helices and its physical properties determined (Table I). This compound has been described (3) but its properties are given again since the values published previously are slightly in error. Backer (1) prepared the *meso*-isomer of this compound, b.p. 141° to 143° C. The *levo*-isomer gives a diphasic azeotrope with water, b.p. 91° C.; the volume of the ketal layer is 3.0 times that of the water.

levo-2,4,5-Trimethyl-2-isobutyl-1,3-dioxacyclopentane

This was prepared from methyl isobutyl ketone and *levo*-2,3-butanediol using 5 ml. of hydrochloric acid per mole of diol. After 2½ hr. the top layer was separated, washed with sodium bicarbonate and distilled with water to separate it from 2,3-butanediol. The ketal–water azeotrope distils at 97° C.; it forms two layers, the volume of the ketal layer being 1.25 times that of the water layer. The ketal was dried with sodium sulphate and refractionated, this gave a colourless liquid, b.p. 120° to 121° C. (200 mm.). Its physical properties are given in Table I (yield, 43% of theory). Equivalent weight (periodate reduction): calc., 86.1; found, 86.3.

levo-2,4,5-Trimethyl-2-amyl-1,3-dioxacyclopentane

This was prepared from *levo*-2,3-butanediol and methyl *n*-amyl ketone using the same procedure as for the isobutyl ketal. The ketal–water azeotrope boiled at 98.5° to 99° C.; the volume of the ketal layer was 0.57 times that of the water. The dry ketal was a colourless liquid, b.p. 143° to 144° C. (200 mm.). The physical properties are listed in Table I (yield, 38% of theory).

levo-2,4,5-Trimethyl-2-phenyl-1,3-dioxacyclopentane

Acetophenone (5 moles) and *levo*-2,3-butanediol (5 moles) were mixed with 25 ml. of hydrochloric acid and warmed to 80° C. for one hour. The mixture was then stirred overnight at room temperature. The ketal was obtained as a colourless liquid; b.p. 146° to 147° C. (93 mm.); yield, 44% of theory. It was refractionated and its physical constants measured (Table I). Its odour is suggestive of violets. Equivalent weight (periodate reduction): calc., 96.1; found, 96.7.

levo-4,5-Dimethyl-2,2-diethyl-1,3-dioxacyclopentane

This was prepared from *levo*-2,3-butanediol (1 mole) and diethyl ketone (1 mole) by treating with 5 ml. of hydrochloric acid and heating to 60° to

70° C. for 30 min. with stirring. This ketal was obtained as a liquid, b.p. 154° to 155° C. (yield, 50% of theory). It was refractionated and its physical constants determined. Equivalent weight (periodate reduction): calc., 79.1; found, 79.7.

levo-3,4-Dimethyl-2,5-dioxa-1-spirodecane

This was prepared from cyclohexanone and *levo*-2,3-butanediol by the general procedure. This ketal is a colourless liquid, b.p. 142° to 143° C. (200 mm.); yield, 78% of theory. It was refractionated through a column packed with glass helices and its physical constants measured (Table I). Equivalent weight (periodate reduction): calc., 85.1; found, 84.9. The *meso*-isomer of this compound was prepared by Backer (1).

levo-2,4,5-Trimethyl-2-(dl-α-hydroxyethyl)-1,3-dioxacyclopentane

Three moles of *levo*-2,3-butanediol were mixed with 3 moles of *dl*-acetoin and sulphuric acid (17 ml.) added dropwise with shaking. The reaction mixture was allowed to stand for four days at room temperature. The product was extracted with ether, some water being added during the extraction to cause formation of two layers. The ketal was obtained as a liquid, b.p. 129° C. (143 mm.); yield, 38% of theory. Its physical properties are listed in Table I. Equivalent weight (periodate reduction): calc., 40.0; found, 40.1. Since this ketal gives a mole of acetoin on hydrolysis it is possible to determine its equivalent weight by measuring the acetic acid formed on oxidation of the hydrolysate with periodic acid. Equivalent weight (acid formed on oxidation with periodate): calc., 160.2; found, 160.8.

dextro-2,4,5-Trimethyl-2-aceto-1,3-dioxacyclopentane and levo-Bis-2,2′-(2,4,5-trimethyl-1,3-dioxacyclopentane)

Diacetyl (3 moles) and *levo*-2,3-butanediol (6 moles) were mixed and 1 ml. of hydrochloric acid added. The mixture was stirred continuously. It heated spontaneously to 50° C. but after one hour two phases had failed to develop so 50 ml. of hydrochloric acid was added. After standing 14 hr. a further 44 ml. of hydrochloric acid was added, the solution warmed to 50° C., and stirred; after 30 min. it became cloudy. The stirring was continued for five hours more. The top layer was then separated and combined with an ether extract of the bottom layer. After washing in the usual manner this was distilled through a two-foot column packed with glass helices. Two new compounds were obtained (*a*) a pale-yellow liquid boiling at 174° C. and (*b*) a colourless liquid boiling at 169° to 171° C. (200 mm.).

The liquid, b.p. 174° C., was washed with water to remove any unchanged *levo*-2,3-butanediol, and redistilled to give an almost colourless liquid, b.p. 134° to 135° C. (200 mm.). (Yield, 13% of theory.) This is the keto–ketal III. Its physical properties are listed in Table I. It forms a hydrazone immediately when treated with 2,4-dinitrophenylhydrazine dissolved in dilute hydrochloric acid whereas all the other ketals only form one after warming (hydrolysis). Found: C, 60.7, 60.5; H, 9.07, 8.97%. Calc. for $C_8H_{14}O_3$: C, 60.7; H, 8.91%. The higher boiling ketal was refractionated to give a colourless liquid, b.p. 170° to 171° C. (200 mm.); yield, 24% of theory. This compound is *levo*-bis-2,2′-(2,4,5-trimethyl-1,3-dioxacyclopentane) (IV). Its physical properties are listed in Table I. Found: C, 62.5, 62.4; H, 9.54, 9.63%. Calc. for $C_{12}H_{22}O_4$: C, 62.6; H, 9.63%.

When an equimolecular mixture of diacetyl and *levo*-2,3-butanediol is treated with a little sulphuric acid a white, crystalline compound is obtained in addition to the liquids described above (yield, about 8%). These crystals dissolve in methanol to give a colourless solution, which turns yellow on boiling. They have an indefinite melting point (65° to 72° C.), which depends on the rate of heating. The melt is yellow but on solidification it again becomes white. On boiling with very dilute sulphuric acid, diacetyl and 2,3-butanediol were obtained in equimolecular yields. This compound may be a monohemiacetal or the combination may be analogous to that of water of crystallization.

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THE CATALYTIC ACTION OF ALUMINIUM SILICATES

I. THE DEHYDRATION OF BUTANEDIOL-2,3 AND BUTANONE-2 OVER ACTIVATED MORDEN BENTONITE[1]

By A. N. Bourns[2] and R. V. V. Nicholls[3]

Abstract

The dehydration of butanediol-2,3 over activated Morden bentonite has been investigated. Below 350° C., liquid products butanone-2, isobutyraldehyde, and the isobutyral of butanediol-2,3 were produced. Butanone-2 was obtained in 86% yield. At higher temperatures, 450° to 700° C., gaseous decomposition occurred. Only small amounts of butadiene were formed from the dry glycol while a 25% diolefin yield resulted using water vapour as diluent. The decomposition of dry butanone-2 over bentonite gave only traces of butadiene. Yields of diolefin increased using water as diluent, 44.8% being obtained at 700° C. with a ketone–water molar ratio of 1 to 40. Butanone-2 was considered intermediate in the formation of butadiene from butanediol-2,3.

Introduction

The fall of the Malay Peninsula, resulting in the loss of almost our entire source of natural rubber, initiated an intensive investigation of all possible methods for the production of butadiene. One of the first methods considered was the dehydration of butanediol-2,3. In Canada, research on the production of *levo*-butanediol-2,3 by the fermentation of wheat mashes by *Aerobacillus polymyxa* was conducted by the Division of Applied Biology of the National Research Council, Ottawa (11). The results of this work indicated that the glycol could be obtained in yields sufficient to warrant a consideration of its use as an industrial chemical.

The investigation reported in this paper deals with a study of the dehydration of butanediol-2,3 in the vapour phase over activated Morden bentonite. Morden bentonite is a Canadian clay mined at Morden, Manitoba, and can be obtained in considerable quantities at a relatively low cost. Previous work in these laboratories had shown that this clay, when activated by treatment with acid, yields an extremely active dehydration catalyst (17). The present investigation was carried out at both low temperatures, giving liquid mono-dehydration products, and at high temperatures, resulting in a decomposition into gaseous products. From preliminary experiments, it appeared likely that the results of the high temperature decomposition might be accounted for by a decomposition of the products of the low-temperature dehydration. Consequently, the investigation was extended to a study of the decomposition of the main low-temperature product, butanone-2, over the bentonite catalyst.

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Contribution from the Division of Organic Chemistry, Department of Chemistry, McGill University, Montreal, Que.

[2] *Graduate student, and holder, at the time, of a Studentship and Fellowship under the National Research Council of Canada. Present address, University of Saskatchewan, Saskatoon, Sask.*

[3] *Associate Professor.*

Previous to the present synthetic rubber program, studies on butanediol-2,3 have been restricted, for the most part, to its mono-dehydration to butanone-2. Langedijk (10), in a review article on butanone-2 in 1938, listed the dehydration of butanediol-2,3 as one of the methods for the production of this ketone. Details of the process were not given, however. Recently, a process has been patented (6) for the liquid-phase dehydration of glycols to aldehydes and ketones, and the dehydration of butanediol-2,3 is given as an example. Akabori (1) investigated the liquid-phase dehydration in the presence of 25% sulphuric acid and obtained isobutyraldehyde in addition to butanone-2. Denivelle (4) carried out the vapour-phase dehydration of the glycol over a variety of catalysts, including sulphuric acid, phosphoric acid, phosphoric anhydride, basic oxides, and zinc chloride, in an attempt to produce butadiene. In all cases, butanone-2 only was obtained. Gutner and Tishchenko (7) passed butanediol-2,3 in the presence of steam over magnesium chloride at 350° C. and obtained a 20% yield of butanone-2 and a 2.9% yield of butadiene. In the absence of steam, the yield of the ketone was 26.2% and of butadiene 4%. Using magnesium sulphate at 300° to 320° C., these workers obtained a 40.6% yield of butanone-2 as well as a 2.6% yield of butadiene.

At the beginning of the present synthetic rubber program, efforts to obtain butadiene directly from butanediol-2,3 were renewed. This investigation was conducted in the United States by the Northern Regional Research Laboratory of the U.S. Department of Agriculture. A report from this laboratory (14) disclosed that 70 catalysts in all had been studied for the direct dehydration of the glycol. One-pass yields of butadiene seldom reached more than 20%, the main product being butanone-2, with methyl vinyl carbinol and butylene oxide as possible by-products. Winfield (18) recently has reported single pass conversions of 60% to butadiene and 80% to butadiene plus butanone-2 by passing the glycol under reduced pressure at 350° C. over thorium oxide.

Very little has been reported on the vapour-phase decomposition of butanone-2 over dehydration catalysts. Mitchell and Reid (12) studied the decomposition of this ketone over silica gel at 500° C. and obtained high boiling condensation products and gaseous products consisting of 15% unsaturated hydrocarbons, 30% methane, 12% carbon monoxide, 15.5% carbon dioxide, and 2% hydrogen. The presence of butadiene was not reported. By the non-catalytic pyrolysis of butanone-2, Hurd and Kocour (8) obtained small yields of ketene and methyl ketene.

Experimental

Materials

Crude *levo*-butanediol-2,3 (produced by the fermentation of wheat mashes by *Aerobacillus polymyxa*) was obtained from the Division of Applied Biology of the National Research Council, Ottawa. This material was diluted with an equal volume of water and heated on a steam-bath for several hours with 200 gm. of calcium oxide per litre of solution to remove any acetic acid

Following filtration, the greater part of the water was removed by simple distillation and the material finally fractionated under reduced pressure through a 3 ft. Stedman column. The physical constants of the purified glycol were: b.p. 177° C. (760 mm.), d_4^{20} 0.992, n_D^{20} 1.4312.

Butanone-2 (methyl ethyl ketone), obtained from the Eastman Kodak Company, was fractionated through a 3 ft. column packed with $\frac{1}{8}$ in. glass helices. The purified material had the constants: b.p. 79.6° C. (760 mm.), d_4^{20} 0.804, $n_D^{15.9}$ 1.3808.

Preparation of Catalyst

Finely powdered Morden bentonite was obtained from the Pembina Mountain Clays Ltd. of Winnipeg. It was activated according to the method of Gallay (5). The material was treated with 20% aqueous sulphuric acid of such a volume that the weight of concentrated acid was 50% of the weight of the clay being activated. This mixture was boiled gently with stirring for three hours. The slurry was diluted to three times its volume, filtered, and the clay washed thoroughly, dried at 110° C. for 12 hr., broken up, and screened to 4 to 8 mesh. After a catalysis run, the catalyst usually carried deposited carbon. This was removed and the activity restored by passing air over the catalyst at 550° to 600° C. for five to eight hours.

Apparatus and Procedure

The apparatus used is shown in Fig. 1. In operation, mercury was fed from the constant-level mercury reservoir, *A*, into a graduated chamber, *B*, containing the liquid under investigation. The rate of flow was controlled by means of a stopcock. By displacement, the liquid was forced into the preheater, *C*, consisting of a 250 cc. flask immersed in an oil-bath, which was maintained at a temperature from 30° to 50° C. above the boiling point of the liquid. The vaporized material then entered the catalyst tube, *D*, consisting of a No. 172 Pyrex resistant glass tube 100 cm. in length and 1.5 cm. inside diameter, contained in a slightly inclined electric furnace. A chromel–alumel thermocouple was placed inside the furnace and immediately outside the catalyst tube. The liquid products were condensed by means of condenser, *F*, and collected in receiver, *G*, while the gaseous products were passed through the bubbler, *I*, and into the gas-meter, *J*. A gas sample for analysis was taken, during the course of a run, into an evacuated gas sampling tube, *K*. In order to ensure equilibrium conditions, a forerun of 15 to 20 ml. was passed before collecting the liquid and gaseous products for analysis. A run usually consisted of 100 ml. of material in addition to the forerun.

Several additional experiments were carried out in the presence of water vapour. Butanediol-2,3 was diluted with the desired amount of water and passed into the preheater from one feeder. Butanone-2 and water, being only partially miscible, were fed from separate feeders. In the case of certain water-vapour runs carried out at fast feed rates, a differently designed apparatus was required to ensure complete vaporization of the material before reaching the catalyst. This apparatus consisted of a 1 in. iron pipe reactor contained in a vertical electric furnace. The upper portion of the reactor was packed with coarse steel wool, which served as the preheater, while the lower portion was packed with the catalyst. The preheater zone was separately controlled and the heat input so adjusted that the vaporized material entered the catalyst zone at the desired reaction temperature. Temperatures were measured by means of two thermocouples, one placed inside the reactor, with the junction immediately above the catalyst zone, and the second placed outside the iron reactor, with the junction about two-thirds up the column of catalyst.

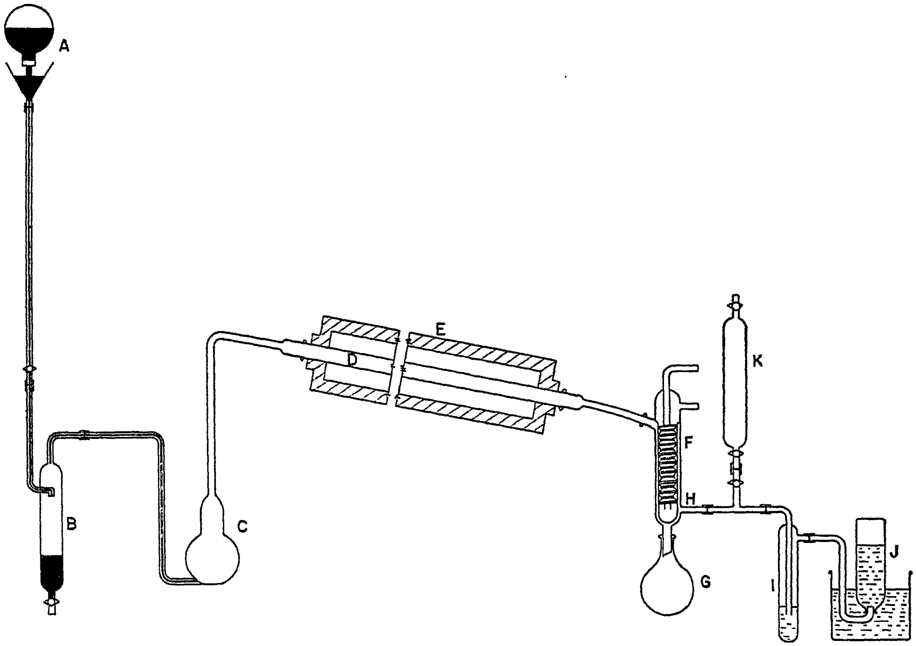


FIG. 1. *Catalysis apparatus.*

Analytical Methods

The liquid products consisted of two layers, an upper organic and a lower aqueous layer. The organic layer was separated, dried, and given a preliminary distillation to remove high boiling material and tarry residue. The product distilling below 150° C. was carefully fractionated through an 18 in. column packed with 3/32 in. glass helices. *p*-Cymene was used as an inert booster. Pure samples of the various components were obtained by combining similar fractions from several runs and refractionating.

The gaseous products were analysed in a modified Bone and Wheeler apparatus. The approximate composition of the gaseous olefins was determined by formation of their dibromides followed by careful fractionation under reduced pressure. *p*-Bromotoluene (b.p. 90° C. (50 mm.)) was used as the booster. The identity of the saturated hydrocarbons was determined by passing the gaseous products, from which carbon dioxide and unsaturated hydrocarbons had been removed, through a series of cold traps. The first was maintained at −80° C. for the condensation of butane and propane, the second maintained at −110° C. for ethane, and the third trap was immersed in liquid air for the condensation of methane. Butadiene was determined volumetrically by absorption in molten maleic anhydride. The apparatus was a modification of that used by Cambron (3).

Results

Dehydration of Butanediol-2,3 in the Absence of Water Vapour

Experiments showing the effect of temperature and feed rate on the dehydration of butanediol-2,3 in the absence of water vapour are given in Table I.

TABLE I

DEHYDRATION OF BUTANEDIOL-2,3 OVER ACTIVATED MORDEN BENTONITE

Run No.	15	16	12	13	3	4	6	7	9
Temperature, ° C.	225	225	275	350	450	550	650	700	700
Feed rate, moles of glycol per hr. per 100 ml. of catalyst	0.635	1.91	1.91	1.91	0.635	0.635	0.635	0.635	1.91
Water formed, moles per mole of glycol	1.01	0.97	1.00	1.02	1.31	1.51	1.39	1.36	1.36
Vapour products, litres per mole of glycol	—	—	—	—	2.59	10.1	21.6	34.2	18.0
Main liquid products, % of theor. yield									
Isobutyraldehyde	3.0	2.6	6.5	12.1	5.7	3.6	1.4	0.5	2.3
Butanone-2	85.0	86.0	83.7	70.1	57.3	39.9	26.9	10.3	36.9
Cyclic acetal	4.7	6.2	2.8	1.7	2.2	2.2	0.8	0.5	0.7
Gas analysis, vol. %									
CO_2	—	—	—	—	17.4	7.3	1.7	1.9	2.1
CO	—	—	—	—	14.7	16.7	27.2	27.2	24.6
H_2	—	—	—	—	0.0	4.1	11.6	14.1	11.5
$CH_2 = CH_2$	—	—	—	—	2.2	3.0	5.0	8.2	6.5
Other unsaturated hydrocarbons	—	—	—	—	43.3	39.1	27.8	20.6	31.5
CH_4	—	—	—	—	3.5	10.4	12.5	17.0	14.9
C_2H_6	—	—	—	—	15.8	17.9	12.5	9.3	8.6
Butadiene in gaseous products, vol. %	—	—	—	—	5.3	4.2	4.2	4.4	7.6
Butadiene yield, % of theor.	—	—	—	—	0.8	2.0	4.1	6.7	6.1

Analysis of the organic liquid products resulted in a separation into four main fractions in addition to a tarry residue. Fraction 1, boiling at 60° to 70° C. (mainly at 64° to 66° C.) consisted of isobutyraldehyde. Fraction 2, collected at 77° to 82° C. (mainly 79° to 80° C.) was practically pure butanone-2. Fraction 3, distilling at 125° to 145° C. with a flat in the distillation curve at 137° to 138° C., consisted mainly of the cyclic acetal formed by the condensation of the glycol with isobutyraldehyde. This compound was identified by synthesis in the liquid phase and by its hydrolysis to butanediol-2,3 and isobutyraldehyde. Fraction 4, distilling at 150° to 250° C., could not be separated into any single component. It was believed to be a complex mixture of high boiling condensation products from butanone-2 similar to that found by Mitchell and Reid when this ketone is passed over silica gel (12). The physical constants obtained for the purified products were as follows:

Isobutyraldehyde	b.p. 64-65° C. (760 mm.)	d_4^{20} 0.798	n_D^{20} 1.3747
2,4-dinitrophenylhydrazone	m.p. 183-183.5° C.		
Butanone-2	b.p. 79.6° C. (760 mm.)	d_4^{20} 0.804	$n_D^{15.9}$ 1.3707
Isobutyral of butanediol-2,3	b.p. 136-139° C. (760 mm.)	d_4^{20} 0.893	n_D^{20} 1.4078

The effect of temperature upon the yields of the major liquid components is shown in Fig. 2.

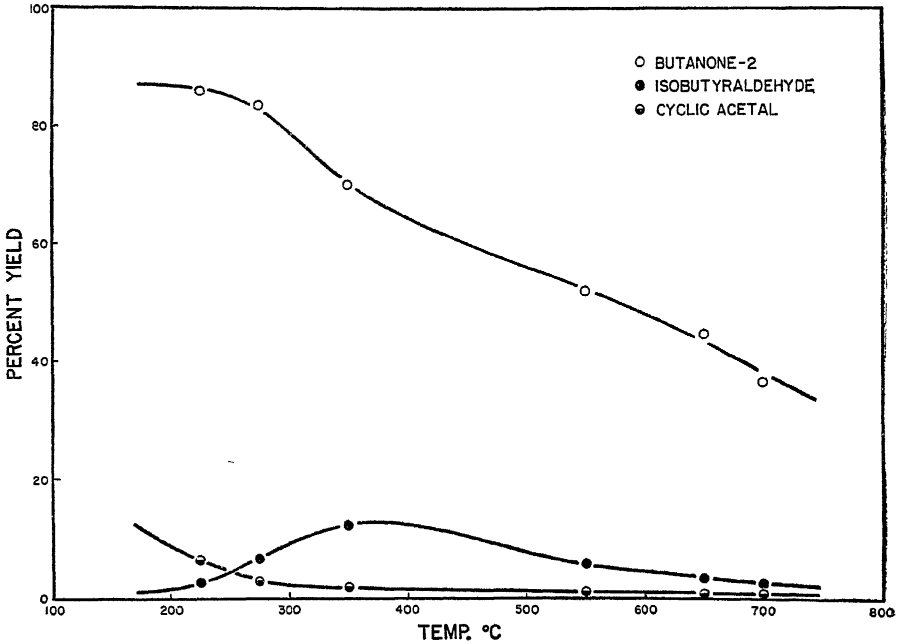


FIG. 2. *The effect of temperature on the yields of liquid products from butanediol-2,3, at a feed rate of 1.91 moles per hour per 100 ml. of catalyst.*

The identity of the olefinic hydrocarbons was determined by fractionation of the liquid dibromides formed from the gaseous products of Run 6. The approximate composition in volume per cent was found to be: ethene 12%, propene 37%, isobutene 21%, and butene-2 (*cis* and *trans*) 30%. Saturated hydrocarbons consisted of methane and ethane only, the amount of each being calculated from data obtained by combustion analysis.

Dehydration of Butanediol-2,3 in the Presence of Water Vapour as Diluent

Experiments showing the effect of temperature, feed rate, and water dilution on the dehydration of butanediol over bentonite are given in Table II.

TABLE II

DEHYDRATION OF BUTANEDIOL-2,3 OVER ACTIVATED MORDEN BENTONITE IN THE PRESENCE OF WATER VAPOUR

Run No.	14	17	75	76
Temperature, ° C.	650	700	700	700
Rate of glycol feed, moles per hr. per 100 ml. of catalyst	0.635	0.635	0.635	0.305
Rate of water feed, moles per hr. per 100 ml. of catalyst	3.18	3.18	6.36	13.71
Vapour products, litres per mole of glycol	10.1	24.5	32.7	25.5
Gas analysis, vol. %				
CO_2	2.5	1.9	5.8	3.6
CO	17.4	17.9	24.2	18.4
H_2	7.7	13.8	14.0	21.8
$CH_2 = CH_2$	5.6	6.5	3.6	3.2
Other unsaturated hydrocarbons	43.4	34.1	31.4	40.3
Saturated hydrocarbons	21.5	23.5	18.1	9.9
Butadiene in gaseous products, vol. %	13.6	7.7	11.6	20.0
Butadiene yield, % of theor.	5.8	8.4	18.8	25.3

The first two runs shown were carried out in the all-glass apparatus, while for Runs 75 and 76 the iron catalysis tube was employed. Organic liquid products were not analysed since their solubility in the large amount of water present made a separation difficult. It is seen that the presence of water greatly increased the butadiene yield, 25.3% of the theoretical being obtained in Run 76.

Decomposition of Butanone-2 Over Morden Bentonite

Experiments showing the effect of temperature, feed rate, and water dilution on the decomposition of butanone-2 are given in Table III. The vertical iron furnace was employed for the experiments involving the use of water to accommodate the faster feed rates. Liquid products were analysed in the case of the dry runs only and were found to consist mainly of water and unchanged ketone. In addition, a small quantity of isomeric pentenes and hexenes and considerable amounts of high boiling material and residue were obtained. It was found that the yield of butadiene increased with increased water dilution. A maximum yield of 44.8% butadiene based on charged ketone was obtained in Run 73, conducted at 700° C. and with a ketone-water molar ratio of 1 to 40. A lower yield in Run 74 with a ketone-water molar ratio of 1 to 60 may have been caused by fluctuations in catalyst temperature due to the fast feed rates involved. Yields based on ketone con-

TABLE III

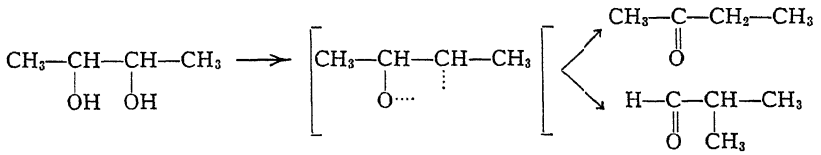
Decomposition of butanone-2 over activated Morden bentonite

Run No.	21	19	22	20	23	71	72	73	74
Temperature, ° C.	450	550	550	650	650	650	700	700	700
Rate of ketone feed, moles per hr. per 100 ml. of catalyst	0.635	0.635	1.59	0.635	1.91	0.635	0.635	0.318	0.318
Rate of water feed, moles per hr. per 100 ml. of catalyst	—	—	—	—	—	3.96	8.72	12.70	19.10
Water formed, moles per mole of ketone	0.20	0.49	0.30	0.45	0.24	—	—	—	—
Vapour products, litres per mole of ketone	2.83	13.4	5.15	26.9	11.5	13.0	24.8	24.8	17.5
Gas analysis, vol. %									
CO_2	43.4	18.2	23.1	5.3	8.0	4.1	2.1	1.7	1.7
CO	12.4	15.3	17.8	15.8	17.8	16.0	18.4	13.7	16.0
H_2	0.0	4.8	1.9	13.1	5.9	5.5	9.4	12.0	16.0
$CH_2 = CH_2$	1.5	2.7	2.3	5.7	5.9	6.9	4.2	2.8	2.9
Other unsaturated hydrocarbons	25.4	28.6	27.7	21.5	21.9	39.2	43.5	52.5	42.0
Saturated hydrocarbons	15.9	30.1	26.1	37.0	35.5	25.5	19.4	15.0	19.8
Butadiene in gaseous products, vol. %	4.3	1.7	3.1	3.7	3.6	12.4	26.3	40.5	33.5
Butadiene yield, % of theor.	0.5	1.0	0.7	4.4	1.8	7.2	29.1	44.8	26.3

sumed were not determined owing to difficulties in separating unchanged ketone from the large volume of water present.

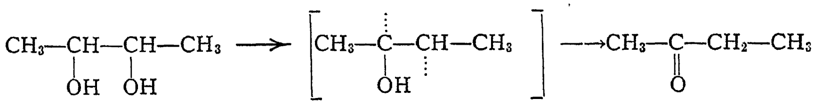
Discussion

Inspection of Table I shows that, at temperatures below 350° C., butanediol-2,3 is dehydrated over Morden bentonite almost entirely into the liquid products, butanone-2, isobutyraldehyde, and the isobutyral of butanediol-2,3. The carbonyl compounds result by a removal of one water molecule from the glycol followed by molecular rearrangement. This may proceed in two ways:

1.


$$CH_3-\underset{OH}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH}}-CH_3 \longrightarrow \left[CH_3-\underset{O\cdots}{\underset{|}{CH}}-\underset{\vdots}{CH}-CH_3\right] \left[\begin{array}{l} \nearrow CH_3-\underset{O}{\underset{\|}{C}}-CH_2-CH_3 \\ \searrow H-\underset{O}{\underset{\|}{C}}-\underset{CH_3}{\underset{|}{CH}}-CH_3 \end{array}\right.$$

This is the so-called pinacolone rearrangement.

2.


$$CH_3-\underset{OH}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH}}-CH_3 \longrightarrow \left[CH_3-\overset{\vdots}{\underset{OH}{\underset{|}{C}}}-\underset{\vdots}{CH}-CH_3\right] \longrightarrow CH_3-\underset{O}{\underset{\|}{C}}-CH_2-CH_3$$

Tiffeneau has called this vinyl dehydration (16). The fact that isobutyraldehyde is also formed does not eliminate the second mechanism since both modes of dehydration may be occurring simultaneously, the first producing ketone and aldehyde, the second forming ketone only.

Akabori (1) obtained both butanone-2 and isobutyraldehyde by distillation of the glycol with 25% sulphuric acid. He suggested that butanone-2 resulted by vinyl dehydration and isobutyraldehyde by a true pinacolone rearrangement.

The isobutyral of butanediol-2,3 is formed by the elimination of water between isobutyraldehyde and the glycol. Backer (2) obtained the cyclic acetal of butanone-2 and butanediol-2,3 by passing the glycol over alumina, while Neish, Haskell, and Macdonald (13) obtained this acetal by treating the glycol in the liquid phase with sulphuric acid.

As shown in Tables I and II, temperatures of 450° C. and higher cause a decomposition of the glycol into gaseous products. Only very small amounts of butadiene are formed when the dry glycol is passed over the catalyst, while the yield of the diolefin is increased when water vapour is used as a diluent. The question arises as to whether the high-temperature gaseous products are formed directly from the glycol or by a further dehydration of the low-temperature liquid products. From a comparison of Tables II and III, it would appear that butanone-2 is intermediate in the formation of butadiene from butanediol-2,3 since, in the presence of water vapour, the diolefin is formed in considerable quantities from both the ketone and glycol. The somewhat lower yields obtained from the glycol may be due to the formation of isobutyraldehyde and other products that are not converted into butadiene.

A two-step mechanism may be suggested for the formation of butadiene from butanone-2. The first step involves the elimination of water to form methylallene, this being followed by a rearrangement to butadiene.

$$CH_3{-}CO{-}CH_2{-}CH_3 \longrightarrow CH_2{=}C{=}CH{-}CH_3 + H_2O$$

$$CH_2{=}C{=}CH{-}CH_3 \longrightarrow CH_2{=}CH{-}CH{=}CH_2$$

Slobodin (15) passed methylallene over floridin at 330° C. and obtained 20.6% butadiene, 3.9% ethylacetylene, and 75.7% unchanged methylallene. Hurd and Meinert (9), on the other hand, have found that a non-catalytic pyrolysis of methylallene at 500° to 550° C. resulted in complete decomposition to carbon, hydrogen, ethane, and propene in 36 sec. The observed effect of water vapour in increasing the yield of butadiene from butanone-2 may be explained on the basis that catalyst contact time has been so reduced that decomposition is hindered and butadiene results by rearrangement.

As far as the authors are aware, this is the first time that the formation of butadiene by the dehydration of butanone-2 has been reported.

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BINARY AND TERNARY EUTECTICS INVOLVING AMMONIUM NITRATE[1]

By A. N. Campbell[2] and A. J. R. Campbell[3]

Abstract

With the object of preparing an 80 : 20 amatol that could be poured, instead of hand-stemmed, the eutectics of many binary and ternary systems, of which ammonium nitrate was one component, have been investigated. It was previously known that ammonium nitrate and sodium nitrate had a eutectic at 120.8° C., a temperature still too high for shell filling, but this binary mixture was frequently used as a basis for the construction of ternary mixtures. The nature of the third component was dictated by practical considerations and varied widely, e.g., alkali nitrate, nitrate of heavy metal, nitrate of organic base, and various organic substances. None of these ternary mixtures was actually used as a shell filling (with trinitrotoluene), though the ammonium nitrate-ethylenediamine dinitrate eutectic, containing 50% ethylenediamine dinitrate and melting at 100° C., comes near to satisfying all requirements; this mixture is entirely non-hygroscopic. Incidental to the work, some interesting phenomena were observed, e.g., the discovery that octadecylamine nitrate forms liquid crystals.

Introduction

The work detailed in this communication was carried out under the auspices of the Associate Committee on Explosives of the National Research Council of Canada. The essential problem was that while 40 : 60 amatols (mixtures of ammonium nitrate and trinitrotoluene) melt to a sludge at the temperature of boiling water, and thus can be readily poured, the 80 : 20 amatol, owing to its low content of trinitrotoluene, forms only a stiff mass under similar conditions, and this has to be charged into shells either by hand or mechanically; this leads to a low charge density.

Our aim was to produce, by admixture, an 80 : 20 amatol that would pour like a 40 : 60 amatol, with corresponding high density. For this purpose we used the binary eutectic ammonium nitrate-sodium nitrate as a starting point. This was shown by Early and Lowry (4) to lie at 20.5% sodium nitrate and a temperature of 120.8° C. This temperature is still too high for shell filling and therefore we studied the addition of various third substances, principally of an oxidizing character, to produce low melting ternary eutectics. For practical reasons, none of these were actually used in shell filling, but the theoretical interest attaching to these ternary eutectics remains.

Experimental

The ammonium nitrate was obtained from the Welland Chemical Works. It had a density of $d_4^{25} = 1.720$, and a moisture content of 0.304%. An analysis accompanying the consignment showed the impurities to be trifling

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[1] *Manuscript received May 16, 1946.*
Contribution from the Department of Chemistry, University of Manitoba, Winnipeg, Man.

[2] *Professor of Chemistry and Head of Department.*

[3] *Wife of the senior author.*

in amount. The technique of the work was thermal analysis in its simplest form. The mixture, completely melted in a large test-tube, was allowed to cool freely, and temperature readings were taken every half-minute. The details of the systems investigated are given below.

AMMONIUM NITRATE – TRINITROTOLUENE

It appeared that the melting point of trinitrotoluene was unaffected by addition of ammonium nitrate, i.e., the liquids are mutually insoluble. This accounts for the formation of a sludge when an amatol is melted, the ammonium nitrate merely remaining suspended in the liquid trinitrotoluene.

AMMONIUM NITRATE – ALKALI NITRATES

Ammonium Nitrate – Sodium Nitrate – Potassium Nitrate

This was an attempt to lower the temperature of the binary eutectic, ammonium nitrate – sodium nitrate (see Introduction) by the addition of potassium nitrate, but the effect was found to be only slight, probably owing to the formation of solid solutions, as mentioned in a previous paper (3). Thus a mixture containing 76.5% ammonium nitrate, 19.65% sodium nitrate, 3.85% potassium nitrate, froze at about 118.5° C., while one of composition 73.5% ammonium nitrate, 19.0% sodium nitrate, 7.5% potassium nitrate, froze at 117.5° C.

A third mixture of composition 72% ammonium nitrate, 20% sodium nitrate, and 8% potassium nitrate, froze at the eutectic temperature of 117.5° C. This temperature is not low enough for shell filling, but we thought this might represent a convenient method of preparing the ammonium nitrate – potassium nitrate solid solutions which are so desirable as a means of preventing the allotropic transformations of ammonium nitrate (3). We therefore investigated whether the above eutectic mixture did or did not exhibit allotropic transformation. Accordingly, a dilatometer was charged with the eutectic mixture and allowed to cool from 130° C. Allotropic transformation, no doubt III $\longrightarrow$ IV, took place at 12° C. Apparently the presence of the sodium nitrate prevents the potassium nitrate exerting its full effect. The explanation is no doubt as follows. It is known that sodium nitrate and potassium nitrate form a continuous series of solid solutions above 130° C. (1). Below this temperature the solid solution breaks up into a conglomerate but the liberated potassium nitrate will not be entirely taken up by the ammonium nitrate, since the system is now largely solid. In other words, the content of potassium nitrate in the ammonium nitrate – potassium nitrate solid solution is less than that which appears from the total potassium nitrate content, and hence the depressing effect on the transition temperature is not so great.

Ammonium Nitrate – Sodium Nitrate – Lithium Nitrate

Lithium nitrate does not form solid solutions with ammonium nitrate (2, 5), and hence this substance had a large effect in depressing the temperature of eutectic crystallization. The lithium nitrate was dehydrated by keeping it in quiet fusion just above its melting point. The following are the results.

Composition of mixture	First appearance of crystals, ° C.	Eutectic temperature, ° C.
16% $NaNO_3$, 21% $LiNO_3$	105	83.7
18% $NaNO_3$, 20.5% $LiNO_3$	113	82.0
16.5% $NaNO_3$, 18.5% $LiNO_3$	106	83.7

The above compositions were chosen by first determining the binary eutectic lithium nitrate–sodium nitrate as lying at 47.0% sodium nitrate and 191° C., and then on a triangular diagram, joining the points corresponding to the compositions of the binary eutectics to the opposite angular points. A small triangle is thus formed whose angular points approximate to the composition of the ternary eutectic. It is apparent that none of the above mixtures is far removed from the ternary eutectic composition. The density of the (molten) mixture containing 18.5% lithium nitrate at 100° C. was found to be 1.61. Mixtures containing lithium nitrate are somewhat hygroscopic.

The Quaternary System: Ammonium Nitrate–Sodium Nitrate–Potassium Nitrate–Lithium Nitrate

A mixture of the following composition: 69.5% ammonium nitrate, 20% sodium nitrate, 8% potassium nitrate, 2.5% lithium nitrate, froze at 116° C. and solidified completely at 110.7° C.

AMMONIUM NITRATE–SODIUM NITRATE–NITRATE OF HEAVY METAL

Systems Containing Zinc or Cadmium Nitrates

Zinc nitrate was found too difficult to dehydrate. The literature regarding the dehydration of cadmium nitrate tetrahydrate is confusing and inaccurate. Anhydrous cadmium nitrate is said to be stable up to its melting point, but this is not true of the hydrated salt, which undergoes hydrolysis much below that temperature (360° C.) when heated under atmospheric pressure. We eventually succeeded in dehydrating cadmium nitrate by the following procedure. The tetrahydrate was heated slowly in an oil-bath, under reduced pressure (steady pumping with a Hyvac) at 80° to 90° C. for two to four hours, for a charge of approximately 100 to 130 gm. hydrated salt. This removed about 80% of the total water of crystallization. The temperature was then raised slowly under constant suction to 140° C., over a period of about two hours; this removed a further 12% of water. Finally the mass was heated, still under suction, to 180° to 190° C. for about one hour, and this removed the last of the water. The binary system ammonium nitrate–cadmium nitrate was first investigated with the following results.

Binary System:—Ammonium nitrate – cadmium nitrate

% $Cd(NO_3)_2$	Freezing temp., ° C.	% $Cd(NO_3)_2$	Freezing temp., ° C.
10% (1)	158.5	30% (2)	119
	158.5		118
	158.0	40 (1)	97–96
10 (2)	159–155	40 (2)	96.5–94.5
20 (1)	140.4	50	98.5
20 (2)	141–137	60	111.5
30 (1)	118.5		

It was found impossible to prepare a clear solution containing 75% cadmium nitrate, as decomposition of ammonium nitrate set in at the high temperature. There are several peculiar features of this system. Although the freezing points are reasonably reproducible, no evidence of a eutectic halt was ever observed; the mixtures became solid at different temperatures, the greater the proportion of cadmium nitrate the lower the temperature. It may be that solid solutions are formed. It may also be that our preparations of dehydrated cadmium nitrate still contained moisture or basic salt, but this does not seem to be borne out by the constancy of the freezing temperatures.

A rough interpolation gives the mixture of lowest freezing point as lying at 46% cadmium nitrate and 84° C.

Ternary System:—Ammonium nitrate – cadmium nitrate – sodium nitrate

Composition		F.p., ° C.	Temp. of complete solidification, ° C.
% $NaNO_3$	% $Cd(NO_3)_2$		
12	42	117.5	113
19.7	3.85	120	117.2
19.0	7.4	119	113.5
17.1	16.65	118.5	107.0

Further work with cadmium nitrate was abandoned because it did not seem possible to produce with any mixture a sufficiently low temperature. In this regard it seems as though the addition of cadmium nitrate alone produces a lower solidification temperature than it does in the presence of sodium nitrate. There are several possible theoretical explanations but, in the absence of further experimental work, it does not seem advisable to go into this. It should be pointed out that between the freezing temperature and the indefinite 'solidifying temperature' the mixture is steadily thickening and becoming less manageable.

Systems Containing Barium Nitrate

Binary System:—Ammonium nitrate – barium nitrate

% $Ba(NO_3)_2$	F.p., ° C.
5	163
7	167
10	189–185

The binary eutectic appears to contain less than 7% $Ba(NO_3)_2$ and to freeze around 163° C., i.e., the depression in freezing point of ammonium nitrate is very slight.

Ternary System:—Ammonium nitrate – sodium nitrate – barium nitrate

Composition		F.p., ° C.	Eutectic, ° C.
% $NaNO_3$	% $Ba(NO_3)_2$		
19.5	5	160	120.3
33.0	4	160.5	120.3

Apparently the presence of barium nitrate hardly affects the eutectic temperature (120.8° C.) of the binary system: ammonium nitrate – sodium nitrate.

System Containing Lead Nitrate

Ternary System:—Lead nitrate – sodium nitrate – ammonium nitrate

Composition		F.p., ° C.	Eutectic, ° C.
% $NaNO_3$	% $Pb(NO_3)_2$		
15	27.5	129.5	111.8
29	23	168	111.5
18	14	122	111.5

AMMONIUM NITRATE – SODIUM NITRATE – ORGANIC SUBSTANCE

Systems Containing Urea

Binary System:—Ammonium nitrate – urea

According to the literature the binary eutectic contains 48.27 mole % of ammonium nitrate and lies at 46.9° C.

Ternary System:—Ammonium nitrate – sodium nitrate – urea

% $NaNO_3$	% Urea	F.p., ° C.	Complete solidification
19.7	3.85	116	Solid at 109
15.5	24.3	89	39.5 (eutectic)
17.7	13.8	101	Solid at 82.3

Systems Containing Urea Nitrate

It was found that the mixtures containing urea were extremely hygroscopic. It was thought that urea nitrate might have a similar effect in depressing the freezing point, without the occurrence of this hygroscopicity.

Binary System:—Ammonium nitrate – urea nitrate

% Urea nitrate, 10; F.p., ° C., 148.

Ternary System:—Ammonium nitrate – sodium nitrate – urea nitrate

Composition		F.p., ° C.
% $NaNO_3$	% Urea nitrate	
19.7	3.85	119
19.7	3.85	118
19.0	7.4*	117
17.65	13.75*	114
16.5	19.3*	109.5
15.5	24.2*	108.5
18.7	7.45*	117.2
17.7	13.8*	114
16.6	19.4*	109.5
15.5	24.3*	108.5

* *All these mixtures effervesce in the liquid state.*

System Containing α-Nitronaphthalene

A molten mixture containing 10% α-nitronaphthalene (90% ammonium nitrate) deposited crystals at 168.5° C. and was sensibly solid at 168.0° C., i.e., molten ammonium nitrate and molten α-nitronaphthalene are mutually insoluble.

Experiments on Hygroscopicity

So many of these mixtures appeared to be highly hygroscopic that a systematic investigation of the matter was undertaken. About 25 gm. of each substance or mixture was exposed to the atmosphere in an open dish and weighed from day to day. The results are contained in the following table. (The weather during the experiments was decidedly humid.)

Substance or mixture	Duration of experiment, days	% H_2O absorbed
1. *NH_4NO_3 alone (dried over H_2SO_4 for a year)	28	0.0
2. $NaNO_3$ alone	28	0.0
3. Urea alone	28	0.0
4. $Cd(NO_3)_2$ anhyd. alone	25	12.55
5. NH_4NO_3–$NaNO_3$ (binary eutectic)	22	9.8
6. NH_4NO_3–$Cd(NO_3)_2$ (binary eutectic)	19	37.7
7. NH_4NO_3–$NaNO_3$ Urea (ternary eutectic)	28	20.9
8. NH_4NO_3–$NaNO_3$–$Pb(NO_3)_2$ (ternary eutectic)	26	16.2
9. NH_4NO_3–$NaNO_3$–$LiNO_3$ (ternary eutectic)	25	29.2
10. NH_4NO_3–$NaNO_3$–KNO_3 (ternary eutectic)	21	11.05
11. NH_4NO_3–$NaNO_3$–$Cd(NO_3)_2$ (ternary eutectic)	19	41.7

* *This result is surprising in view of the notorious hygroscopicity of ammonium nitrate. During the first part of the month, when the weather was very humid, the ammonium nitrate did increase in weight by 0.085%, but it lost this as the atmosphere dried up again. We are inclined to doubt whether absolutely pure ammonium nitrate is hygroscopic. It has always been thought to be so, but only since the advent of the Haber and similar processes has really pure ammonium nitrate been obtainable commercially.*

It is noteworthy that while the components themselves are not appreciably hygroscopic (with the exception of cadmium nitrate), the binary eutectics are very hygroscopic, and the ternary eutectics still more so. This is connected with the lowering of the melting point.

Systems Containing Phenol

Phenol is known to form a compound with urea having the composition 2 moles phenol: 1 mole urea, and this compound, having an incongruent melting point, is completely dissociated in the liquid state. It was thought that the dissociated urea might, in the liquid state, exert its powerful depressing effect on the melting point of ammonium nitrate, while, after solidification, the phenol might unite with the urea to form a non-hygroscopic mixture. The first question to investigate was whether this compound of 2 phenol: 1 urea was itself hygroscopic. So far from being hygroscopic, the compound, on prolonged exposure to the atmosphere, lost weight slowly but steadily, probably owing to volatilization of the phenol.

Binary System:—Ammonium nitrate – 2 phenol: 1 urea

% Phenol–urea	F.p., ° C.	Eutectic
10	159.5	All solid at 145.0° C. except for layer of liquid phenol.
55	115	Lower layer solid at 105° C.

This device failed because the gravitational separation of the dissociated phenol gave rise to two liquid layers.

Ammonium Nitrate – Ethylenediamine Dinitrate

The purity of the ethylenediamine dinitrate was estimated by distillation with sodium hydroxide and collection of the distillate in standard acid, followed by back titration with standard alkali. Purity = 99.5%.

Equilibrium Diagram. System:—Ammonium nitrate – ethylenediamine dinitrate

Wt. % E.D.D.	Freezing point, °C.	Eutectic temperature, ° C.
10	151	Solid at 132
20	137	Allotropic transformation at 124; stirring ceased at 105
30	122	97.3
40	110	97.3
50	98.2	96.8
50 (repeat)	100.2	103
	101.7	104
60	112.5	102.1
80	135.5	Solid at 124.5
90	148	Obvious decomposition of ethylenediamine dinitrate.

The thermal determination of the eutectic temperature is seen to be rather hazy. When the freezing point curves are plotted, the diagram is seen to be of simple eutectic form (absence of compound formation), the eutectic lying at 50% ethylenediamine dinitrate (by weight) and about 100° C. A direct investigation of a freshly prepared 50% ethylenediamine dinitrate gave crystals at 99.0° C., followed by a rise to constant temperature at 102.5° C. This therefore may be taken as the true eutectic temperature.

Hygroscopicity of Ammonium Nitrate–Ethylenediamine Dinitrate Eutectic

After 18 days' exposure to the atmosphere, the increase in weight amounted to 0.0089%.

The System:—Ethylenediamine Dinitrate–Trinitrotoluene

The melting point of trinitrotoluene is unaffected by the presence of ethylenediamine dinitrate; in other words, the liquids are mutually insoluble.

Effect of Ethylenediamine Dinitrate on Allotropic Transformations of Ammonium Nitrate

It was possible, despite the eutectic form of the equilibrium diagram, that ethylenediamine dinitrate might form solid solution with ammonium nitrate and thus affect its transition points. Accordingly, this point was investigated dilatometrically.

A mixture of 10% ethylenediamine dinitrate and 90% ammonium nitrate was melted at 180° C., poured into a mortar, cooled, and ground. Thirty-five grams of this mixture was placed in a dilatometer having a wide capillary so that the whole range of transitions could be investigated without refilling. The indicator fluid was xylene. The completely filled dilatometer was heated at 120° C. for half an hour to ensure equilibrium. The temperature was then allowed to fall, the position of the meniscus being followed, to room temperature. The measurements were then repeated with rising temperature.

1. *Falling temperature* *Transitions at:—*
66.5° C. II → III
27.5° C.} III ⇌ IV
2. *Rising temperature* 37.0° C.} Mean = 32.25° C.

From this it is concluded that ethylenediamine dinitrate has no effect on the transitions:—IV ⇌ III and III ⇌ II. The thermal analysis showed that the transformation II ⇌ I, at 124° C., is not affected. Hence ethylenediamine dinitrate does not form solid solutions with ammonium nitrate.

Density of solid ethylenediamine dinitrate at 25° C.

d_4^{25} = 1.598, 1.593: mean = 1.595

Density of solid eutectic (50% ethylenediamine dinitrate)

d_4^{25} = 1.631, 1.635: mean = 1.633

*Cyclohexylamine Nitrate**

Equilibrium Diagram:—Ammonium nitrate – cyclohexylamine nitrate

10% Cyclohexylamine Nitrate. This mixture decomposed with charring below its melting point.

20% Cyclohexylamine Nitrate. Mixture decomposed below its melting point. When it was heated all night at 110° C. there was no sign of melting. The pure cyclohexylamine nitrate also decomposed at its melting point. The density was determined as $d_4^{25} = 1.204$.

Octadecylamine Nitrate

The behaviour of this substance on melting is very peculiar. Heated at the temperature of boiling water, it shrank to a paste. When the temperature was then raised to 150° C., the paste expanded to form a rubber-like mass, which became slightly yellow on cooling. We suspected the formation of liquid crystals, and accordingly an examination was made with a polarizing microscope on a heated substage. Under polarized light, there appeared to be slight movement of the crystals at 71° C.; at 76.4° C., portions of black field then appeared, interspersed with crystalline fragments. The interference persisted at 88° C. Under ordinary light at this temperature, the molten masses still showed an irregular outline, reminding one of crystals. The substance decomposed at 160° C. On cooling the isotropic liquid, interference reappeared between 70° to 90° C., in different experiments. I suggested to Dr. Downing that further investigation along these lines should be undertaken by the Crystallographic Department at Cornell. This was done and Dr. Blomquist reported as follows, in qualitative agreement with our findings.

"The compound *n*-octadecylamine nitrate which you so kindly sent us has proved to be extremely interesting. We have made some studies of the material on the hot stage microscope and by fusion analysis and have observed some interesting crystal properties. The substance exists in two solid polymorphic forms and in a liquid crystal form. All of the polymorphic transformations are reversible by temperature variation.

"On melting at 80° C. liquid crystals are formed. These appear between crossed Nicols as feathery crystals but are invisible in the liquid in the ordinary light. On making the liquid flow by moving the cover glass, the liquid crystals change shape and appearance. By pushing down on the cover glass the liquid crystals line up so that one looks down BX_a, thus the interference figure has been obtained and shows the optic axial angle, 2V, to be about 15° with slight dispersion.

"On cooling, the liquid crystals transform to a true solid modification at about 80°. The transformation is reversible. This solid modification shows very low birefringence. Mottled areas of random crystal orientation show first order grey and white. A few areas show an imperfect optic axis interference figure. 2V is in the range 70° – 90° C.

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* *We are indebted to Mr. E. Pritchard for the experimental work on cyclohexylamine nitrate.*

"Further cooling to 70° brings about another reversible transformation to the low temperature stable modification. This is a solid-solid transformation. The low temperature form appears as feather-like interlaced crystals having higher birefringence than the first solid. The small crystal size and the interlacing of other crystals make it possible to obtain good interference figures."*

Equilibrium Diagram:—Ammonium nitrate – octadecylamine nitrate

Pure octadecylamine nitrate: Freezing point = 76.1° C. (very indeterminate because of the rubber-like nature of the mass).

10% Ammonium nitrate F.p = 74.0° C. (very approximate)
20% Ammonium nitrate F.p. = 73.0° C. (uncertain)
72.3° C.
40% Ammonium nitrate F.p. = 72.3° C.

There was no indication of eutectic freezing in any of the above melts. We deduce that the solubility of ammonium nitrate in molten octadecylamine nitrate is slight.

A mixture of trinitrotoluene and octadecylamine nitrate containing 10% octadecylamine nitrate froze at the freezing temperature of pure trinitrotoluene, viz. 79.3° C. Hence, octadecylamine nitrate is insoluble in molten trinitrotoluene.

Density: $d_4^{25} = 1.044$.

Further work was abandoned because (i) octadecylamine nitrate and ammonium nitrate are mutually insoluble, or almost so; (ii) the rubber-like nature of the molten mass renders it difficult to handle; (iii) the density is extremely low.

Summary

The composition and temperature of the different eutectics are given in the following table.

System	Eutectic temp., ° C.	Eutectic composition
NH_4NO_3–T.N.T.	Same as m.p. of T.N.T.	Mutually insoluble
NH_4NO_3–$NaNO_3$	120.8	20.5% $NaNO_3$ (4)
NH_4NO_3–$NaNO_3$–KNO_3	117.5	Unknown because of formation of solid solution.
$NaNO_3$–$LiNO_3$	191	47.0% $NaNO_3$
NH_4NO_3–$NaNO_3$–$LiNO_3$	83.7	16.5% $NaNO_3$, 18.5% $LiNO_3$
NH_4NO_3–$Cd(NO_3)_2$	84†	46% $Cd(NO_3)_2$†
NH_4NO_3–$Ba(NO_3)_2$	160	Less than 7% $Ba(NO_3)_2$
NH_4NO_3–$NaNO_3$–$Ba(NO_3)_2$	160	Less than 5% $Ba(NO_3)_2$
NH_4NO_3–$Pb(NO_3)_2$	111.5	Not known
NH_4NO_3–Urea	46.9	48.27 mole % NH_4NO_3
NH_4NO_3–$NaNO_3$–urea	39.5	Not known
NH_4NO_3–$NaNO_3$–urea nitrate	108.5†	15.5% $NaNO_3$, 19.3% urea nitrate†
NH_4NO_3–ethylenediamine dinitrate	100	50% ethylenediamine dinitrate

† *Very approximate.*

* *Dr. Blomquist asks us to state that "the crystallographic work was actually carried out by Dr. W. C. McCrone, who was working under my direction."*

The above table does not contain all the systems investigated, because, for experimental reasons such as decomposition, formation of solid solutions, etc., it was not always possible to evaluate the eutectic conditions.

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MEASUREMENTS OF CURE OF SOME THERMOSETTING RESINS[1]

BY MANUEL N. FINEMAN[2] AND IRA E. PUDDINGTON[3]

Abstract

The rate and degree of cure of resorcinol–formaldehyde resins and unsaturated polyesters are determined by measuring changes in their electrical resistance and density during the process of cure. Data thus obtained are interpreted in terms of the rate and extent of cross-bonding in these thermosetting resins.

Introduction

In a previous publication (1), a method for determining the rate and extent of cure for thermosetting resins of the cast phenolic type was described. This method consisted eassentially in measuring changes in the electrical resistance of the resin during the curing cycle. Since, on curing, thermosetting resins change from liquids of low viscosity to gels and finally become three-dimensional in structure, their electrical resistance increases over a very wide range until, as solids, the resins become good dielectric materials. Data thus obtained were correlated with measurements of changes of density with time of cure.

The electrical measurements were shown to be sensitive to changes in the internal molecular arrangement of these systems, such as rate and extent of cross-linkage formation, while the density determinations were mainly charateristic of macro properties. The increased rate of cure as a result of rising temperature or added accelerator and retarding effect of plasticizers were indicated by the results obtained.

In the present paper an attempt has been made to apply this procedure to other thermosetting resins such as resorcinol–formaldehyde and unsaturated polyesters. The results obtained with these materials are reported below and confirm the usefulness of this procedure in indicating experimentally the rate and extent of cross-bonding in thermosetting resins of this type.

Experimental

Preparation of Samples

Resorcinol–formaldehyde resin was prepared by mixing 125 gm. of formaldehyde (37%, U.S.P.) with 110 gm. of resorcinol (U.S.P.) kindly supplied to us by the Pennsylvania Coal Products Co. of Petrolia, Pa. These quantities represent a molar ratio of approximately 1 : 1.5 of resorcinol to formaldehyde, and the solution had a pH of about 3.0. By careful addition of small

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[2] *Chemist. Present address: Department of Chemistry, Stanford University, California.*

[3] *Chemist.*

quantities of a sodium carbonate solution to this mixture, two other resin solutions were prepared with a pH of 5.5 and 7.0, respectively.

The unsaturated polyester used in these experiments was a commercial product of the American Cyanamid Co. known as Laminac 4122. It is an almost water-white liquid thermosetting resin, which is 100% reactive. As it is chemically unsaturated, a small quantity of peroxide catalyst was used to activate its rapid conversion to a solid, which proceeds without the formation of by-products. The catalyst used was technical lauroyl peroxide distributed by the Lucidol Corp. under the trade name of Alperox C.

Apparatus

The cells in which the resistance measurements were made were constructed of concentric copper tubing, the resin being poured into the annular space between these tubes. A General Radio Capacitance Bridge, Type 716-B, was used for the electrical measurements. For the density determinations, glass dilatometers were constructed using mercury as the displacement liquid and a horizontal capillary for measuring the changes in volume as the resin cured. This apparatus has already been described in detail (1).

Results

Fig. 1 shows the results obtained on curing resorcinol–formaldehyde resin at room temperature (i.e., 25° ± 2° C.). Plotting electrical resistance logarithmically against time of curing, Curve *A* represents the behaviour of a resin of pH 3.0; Curve *B*, of pH 5.5; and Curve *C*, of pH 7.0. The points that deviate from the curves are due to fluctuations in the room temperature that were later eliminated in the density experiments by the use of a thermostatically controlled water-bath. The resin of pH 7.0 cured very rapidly immediately after formation, with the evolution of a large quantity of heat which further speeded the reaction, causing boiling inside the resin and the formation of a very porous solid. In order to prevent too rapid cure, the resin represented by Curve *C* was cooled by running water for the first hour after preparation and then poured into the resistance cell. Thereupon cure took place at a more moderate rate, continuing for several days. Fig. 1 shows that the slope of the curve and extent of change of the electrical resistance increase very rapidly as the pH of the resin is increased.

Fig. 2 shows the behaviour observed for the polyester casting resin, Laminac 4122, when cured in a constant temperature oil bath at 80° ± 0.1° C. Curve *A* represents the behaviour of the polyester with 0.5% of added catalyst; Curve *B*, with 0.3%; and Curve *C*, with 0.1%. The initial rapid drop common to the three curves represents the drop in resistance as the samples warmed up from room temperature to the temperature of the oil-bath. Then, for the first few hours of cure, the electrical resistance increased very rapidly as the samples quickly changed from a liquid of about 200 centipoises viscosity to a hard solid. Subsequently the graph shows that the electrical resistance of the resin with 0.1% of added catalyst increased much less with time than that of either of the two other samples whose behaviour was almost identical.

The resistance data reported in Figs. 1 and 2 are for samples of 57.0 gm. weight, measured in cells whose dimensions were identical, as previously described (1). Thus the values obtained may be assumed to be directly comparable even though they are not reduced to read in terms of specific resistance.

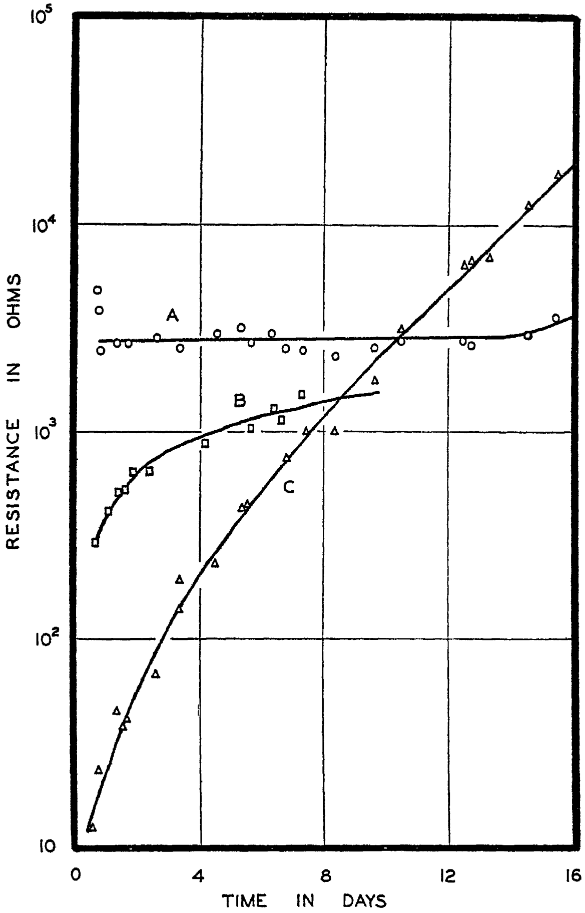

FIG. 1. *Change of electrical resistance with time of curing. Curve A, resorcinol–formaldehyde resin of pH 3.0; Curve B, of pH 5.5; and Curve C, of pH 7.0.*

In Fig. 3 the density data are reported for both the resorcinol–formaldehyde and the polyester resins. For these experiments the dilatometers were immersed in constant temperature baths that did not vary more than ± 0.1° C. The temperature of cure was 25.0° C. for the resorcinols and 80.0° C. for the polyester resin.

Curves *A* and *B* represent the changes in density with time of cure for the resorcinol resins of pH 3.0 and 5.5, respectively. Despite the marked difference in their electrical behaviour as shown by Curves *A* and *B* of Fig. 1, the density data show that the resin of higher alkalinity displays only a slightly greater degree of shrinkage than does that of lower alkalinity. After about five to eight days of curing, these resins started to exude from 5 to 10% of water, thus making subsequent density calculations inaccurate. The resorcinol sample of pH 7.0 cured too rapidly to give accurate results in the dilatometer.

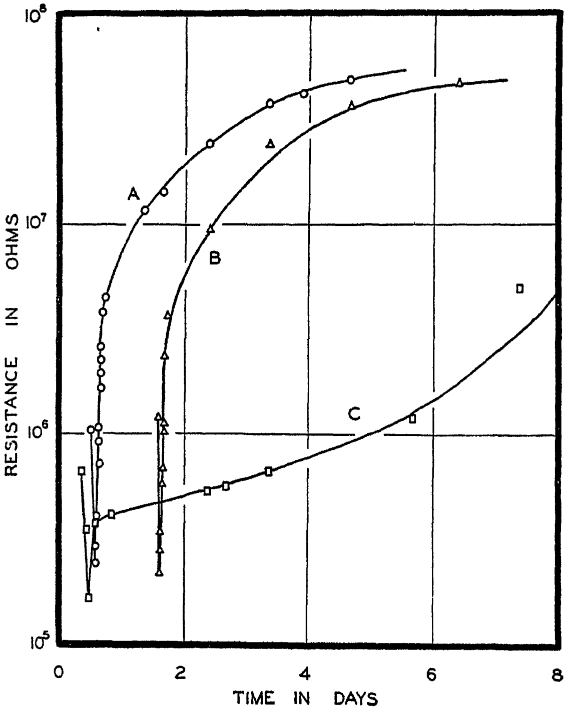

FIG. 2. *Change of electrical resistance with time of curing. Curve A, polyester with 0.5% of added catalyst; Curve B, with 0.3%; and Curve C, with 0.1%.*

Curve *C* of Fig. 3 describes the density change observed for a polyester sample at 80° C. to which 0.1% of catalyst had been added. It will be noted from the scale of the abscissa that the density change takes place very rapidly after an initial time lag—much more rapidly than in the case of the resorcinols. This time lag was partly the time required to bring the sample up to the temperature of the bath.

Where this curve shows its greatest slope, two regions are indicated over which low density values were recorded. This was probably due to the formation, at the mercury surface, of a resin-to-glass seal that did not rupture until considerable shrinkage had taken place in the body of the resin, thus preventing the accurate recording of the density change. Polyesters with a catalyst concentration of 0.3% or higher shrank even more rapidly than the sample whose density behaviour is here described. Hence no reliable data for these were obtained.

Discussion

Assuming that the passage of current through these samples depends upon the free mobility of any ions that may be present in the system, steric factors, such as the formation of cross-bonds, might be expected to restrict this property (2, p. 168). Therefore, the electrical resistance of these samples will increase continuously as the number of cross-linkages in the system increase.

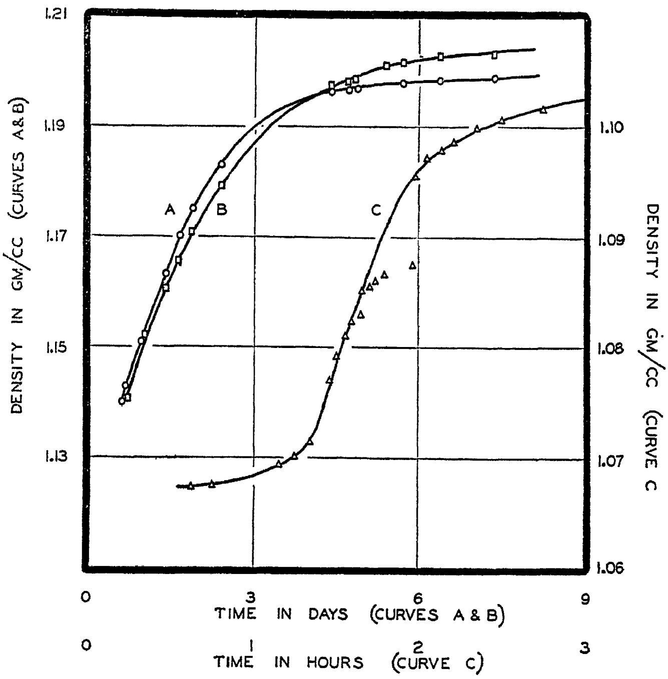

FIG. 3. *Change of density with time of curing. Curves A and B, resorcinol-formaldehyde resin of pH 3.0 and 5.5, respectively; Curve C, polyester with 0.1% of added catalyst.*

Hence the rate and extent of cross-bonding, which represents the rate and degree of cure of these materials, can be compared by measuring the changes in the electrical resistance of the samples as condensation or polymerization proceeds.

Bearing this mechanism in mind, Curve *A* of Fig. 1 would seem to indicate that very few, if any, cross-bonds are formed in a resorcinol resin of low pH. However, as the alkalinity of the resorcinol resin increases, so too does the rate of cure and the number of cross-linkages formed.

The curves of Fig. 2 can also be interpreted on this basis on the assumption that 0.1% of peroxide catalyst is not sufficient to give 100% reaction during the time of observation. Hence Curve *C* shows a much lower electrical resistance than that attained by the two other samples. In each of the latter, cross-linkage formation must have been virtually complete and hence the two curves are almost identical in shape. It may be noted that 0.3% of catalyst is the amount recommended by the manufacturer for use under the conditions of this experiment.

With the setting up of cross-bonds, the molecules of the resin become oriented more closely together in space and occupy a smaller volume. This behaviour is demonstrated by Curves *A* and *B* of Fig. 3, which describe the curing of the resorcinol resins. As previously shown by the electrical measurements, it will be noted that here, too, the density change is slightly greater for the resin of higher alkalinity. According to the more recent theories governing the mechanism of condensation of phenols and resorcinols with formaldehyde, it has been generally accepted that, for a given resin in which normally very few cross-linkages are set up, this number can be increased by increasing the concentration of hydroxyl. In alkali, methylol groups are formed that assist in the formation of cross-linkages (3, 4). A similar case involving phenol–formaldehyde resin of molar ratio 1 : 0.8 has already been discussed (1).

Curve *C* of Fig. 3 shows that the greatest change in density for the polyester sample takes place during the first few hours of cure; this corroborates the electrical data (Curve *C*, Fig. 2), which indicate that the largest change in electrical resistance occurs during the first few hours. Moreover, although these samples may reach what appears to be a maximum density after the first few hours of cure, the electrical curves indicate that polymerization continues for several days until the maximum number of cross-bonds possible for the system are set up. This is further suggested by the fact that both Curves *A* and *B* of Fig. 2 become asymptotic to the abscissa at about the same value of the resistance, i.e., about 5×10^7 ohms.

It might be supposed that the shrinkage of the resin on curing may have caused deterioration of the contacts at the resin–electrode interface in the cylindrical cell. Any such deterioration could give rise to an increase in the measured electrical resistance. To investigate this further, a sample of the polyester was cured at 80° C. with added catalyst, using two probe electrodes immersed in the resin, instead of the cylindical cell. In this case, shrinkage of the resin could only improve the contacts. The results observed were analogous to those obtained when the cylindical type of cell previously described was employed. This has also been confirmed in the case of resol resins (1). Furthermore, it should be pointed out that the resorcinol resin of pH 3.0, which showed a marked shrinkage during the first five days of cure (Curve *A*, Fig. 3), did not show a rise in electrical resistance until after 15 days (Curve *A*, Fig. 1). These observations seem to confirm the view that the electrical data observed were not a result of deterioration at the resin–electrode interface.

It might also be suggested that loss of water by the resin during the curing process gave rise to the changes in electrical resistance that were observed. However, in the case of the polyester resin, 100% reaction is said to be obtained without the formation of by-products. That is, the curing process was one of polymerization, not condensation, and hence no water was present.

Thus it may be concluded that the changes in electrical resistance and density shown by thermosetting resins during cure are real functions of the degree of advancement of these resins and may be interpreted in terms of the mechanism of cross-linkage formation.

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CATALYTIC AROMATIZATION OF TURNER-VALLEY CRUDES[1]

W. GRAHAM[2], A. T. HUTCHEON[2], AND J. W. T. SPINKS[3]

Abstract

The maximum yield of toluene resulting from catalytic aromatization of a selected cut from Turner Valley crude oil has been determined. Using a catalyst containing 14% chromium trioxide on aluminium trioxide and a temperature of 515° C., a total yield of toluene equal to 3.15% by weight of the original crude may be obtained. This is 137% greater than the quantity of toluene originally present in the crude (1.33%). A possible recovery of approximately 250,000 lb. of toluene per day is indicated for the whole Turner Valley field (1942).

Introduction

It is a well known fact that North American crude oils contain a relatively small percentage of aromatic hydrocarbons (18, 27). Fortunately however, these same crude oils contain appreciable amounts of aliphatic hydrocarbons which may be catalytically converted to aromatic hydrocarbons.

A rough calculation on one of the Turner Valley crudes (Foundation well No. 1; see (27)) indicates, for example, that heptane and 2- and 3-methylhexane are present in sufficient quantity to yield 2.9% toluene (based on the original crude) by catalytic aromatization. The original toluene content of this particular crude was 1.07%, and thus an increase in the toluene yield of about 160% might be expected to result from an efficient catalytic operation.

In recent years a number of studies have been made on the catalytic conversion of aliphatics to aromatics (see, for example, 3, 6, 9, 13, 15–17, 19–21, 23–25). From these studies it appears that:

(1) A number of oxides act as efficient aromatization catalysts, chromium trioxide and vanadium pentoxide being the most active;

(2) The oxides are usually supported on alumina;

(3) Mixed oxides of chromium, molybdenum, and vanadium, on alumina, give a catalyst superior to chromium trioxide on alumina;

(4) A high conversion of aliphatics to aromatics is favoured by a temperature of about 500° C. and a low feed rate;

(5) Hydrocarbons whose structure permits direct formation of a six carbon ring are aromatized to a marked extent, whereas hydrocarbons whose structure does not permit direct formation of a six carbon ring are not appreciably aromatized.

Considerable increases in the yields of aromatics from petroleum cuts as a result of catalytic aromatization have already been reported (14, 16, 28) and

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Contribution from the Department of Chemistry, University of Saskatchewan, Saskatoon, Sask.

[2] *Graduate student.*

[3] *Professor of Physical Chemistry.*

it was thought worth while to do similar work on Turner Valley crudes, particularly as information concerning the aromatic content of some Turner Valley crudes was already available in this laboratory (11).

Experimental

Apparatus

The apparatus is illustrated in Fig. 1 and is similar to that described by Hoog, Verheus, and Zieuderweg (13). The liquid feed was vaporized at 200° C. in a preheater and the vapour passed over the catalyst. The catalyst was contained in a Pyrex tube heated in a vertical block furnace to 500° C. The product was condensed in a trap immersed in a dry-ice–acetone mixture. Any uncondensed gas was collected in a gas holder. A sample of the gas was usually analysed.

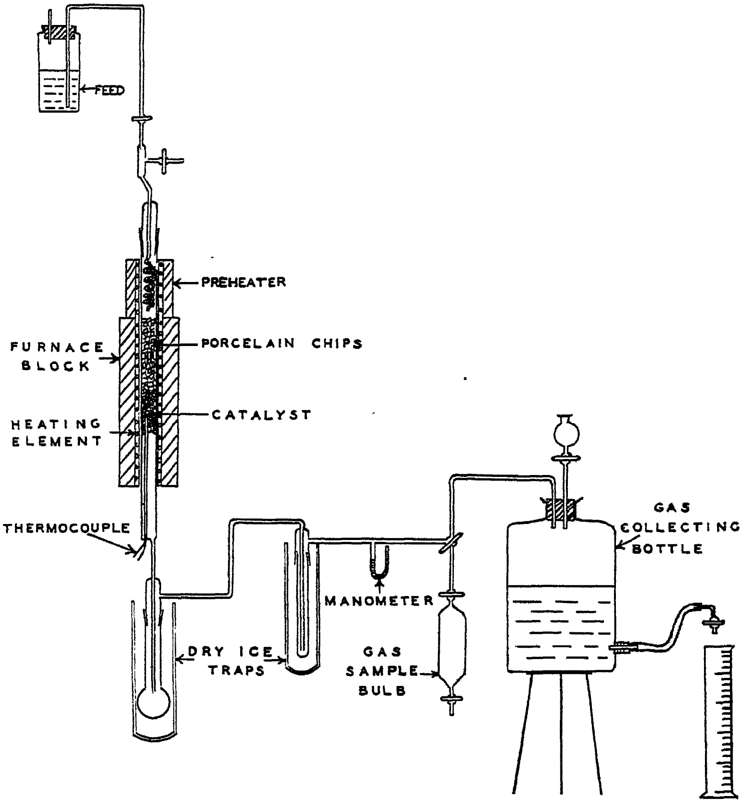

FIG. 1. *Apparatus for cyclization.*

Catalyst

Catalysts 1 and 2. The catalyst was prepared as outlined by Grosse, Morrell, and Mattox (9). Eight-mesh granules of activated alumina (Aluminum Co. of America) were impregnated with chromium nitrate solution, dried for several hours at 100° C., and finally heated to 400° C. for four hours.

Catalyst No. 1. 4.5% Chromium trioxide on activated alumina.

Catalyst No. 2. . 7.0% Chromium trioxide on activated alumina.

Catalyst No. 3. Aluminium trioxide was prepared according to Adkins, (1, 2).

Aluminium nitrate nonahydrate (300 gm.) was dissolved in 2 litres of water. The solution was heated to boiling and concentrated ammonium hydroxide solution added until precipitation was complete. The solution was diluted to 4 litres, heated to boiling for 15 min., and allowed to cool. The precipitate was washed with distilled water and centrifuged. The precipitate of aluminium hydroxide was dried, first at 100° C. and then at 500° C. to give alumina. The dried particles were about 4 to 8 mesh in size. These particles were impregnated with chromium nitrate solution to give a catalyst containing 8.3% chromium trioxide.

Catalyst No. 4. 9.7% Chromium trioxide on activated alumina.

Catalyst No. 5. 14.2% Chromium trioxide on activated alumina.

The catalyst was usually revivified after each experiment. The procedure was to flush with nitrogen, then with air at 500° C. for three hours, then with nitrogen, then with hydrogen for three hours, and finally with nitrogen (8, 22, 25).

Analysis

(a) Liquid Product

The liquid product was analysed for aromatics by the dispersion method (10, 11, 26). The base values were checked from time to time and the dispersion method itself was rechecked with the nitration method (4) on several toluene cuts (b.p. 88° to 119° C.) from Turner Valley crudes. The base value of the aromatized material was determined in the usual way and was found to be the same as for the original feed.

Sample	Toluene in toluene cut, %	
	By nitration	By dispersion
Home Millarville 2	12.9	13.8
Royalite 31	18.8	18.8
Royalite 43	20.3	20.5

The liquid products were also analysed for olefins by the Francis method (7). The method was tested on pure cyclohexene, prepared by dehydration of cyclohexanol on activated alumina (12, p. 27). Bromine numbers of 194.9 and 193.6 were obtained; theoretical, 194.

Conjugated diolefins were tested for by the Diels–Alder reaction following the procedure of Grosse and Wackher (10). No significant amounts of conjugated diolefins were found, in agreement with results in similar cyclization experiments performed elsewhere.

(b) Gaseous Products

The gaseous products were analysed for carbon dioxide, oxygen, unsaturates, hydrogen, and carbon monoxide, on a modified Orsat apparatus (5). A typical gas analysis is recorded below, together with one by Taylor and Turkevich (24). Both runs were made with heptane at 515° C. using a chromium trioxide catalyst.

Constituent	Gas analysis, volume, %	
	Run No. 31	T. and T.
CO_2	0.0	0.12
Unsaturates	0.9	0.84
O_2	0.3	0.23
H_2	86.5	87.6
CO	0.6	0.73

Materials

The following materials were used in catalytic dehydrogenation experiments:

I. Hexane (Eastman), Pract.; b.p. 62° to 68° C. $d_4^{20} = 0.6621$; $n_d^{20} = 1.37567$.

II. Heptane (Eastman), Pract.; b.p. 92° to 96° C. $d_4^{20} = 0.7158$; $n_d^{20} = 1.40232$.

The heptane contained a small percentage of aromatics, which was removed by nitration. After nitration n_d^{20} was 1.39678. A true boiling curve of the heptane indicated that this material actually contained less than 40% heptane. However, it was thought that this material would show a behaviour somewhat similar to that for the toluene cut (90° to 120° C.) from Turner Valley crude, and consequently it was used in preliminary experiments to determine the effect of feed rate, temperature, and catalyst composition on the yield of aromatics.

III. Heptane (Eastman), pure; $n_d^{20} = 1.38776$.

In order to determine possible yields of toluene from Turner Valley crudes, toluene cuts were used which had been freed from toluene by nitration.

IV. Nitrated Toluene cut *(a)* from Turner Valley crudes.

One-litre portions of crude from three Turner Valley wells were fractionated in a 3 ft. Stedman column. The toluene cuts (b.p. 90° to 120° C.) were nitrated to remove any aromatics. The nitrated portions were washed and dried and used as feed in Runs 9, 12, and 13 (see Table IV).

V. Nitrated toluene cut *(b)* from Turner Valley crudes.

Thirteen litres of Turner Valley crude oil (equal volumes of Foothills 6, Home Millarville 2, and Royalite 31) were distilled in a 2-in. steel column. The cut from 70 to 130° C. was retained (1650 cc.). This cut was distilled in a 5 ft. Stedman column (1-in. diameter), product being removed at 20 cc. per hour. The cut from 90° to 120° C., hereinafter called the toluene cut, was collected; it measured 1066 cc. From previous experience, we can say that this cut contains all the toluene, together with the hydrocarbons which will cyclize to toluene (without cracking). Four hundred cubic centimetres of this cut was nitrated to remove aromatics (called nitrated toluene cut) and was used in aromatization runs Nos. 45 to 56 (see Table VI).

The following data, obtained on the toluene cut, indicate that the original crude contained 1.33% toluene by weight.

	Density	δ^{20}_{g-e}*	Aromatics (dispersion), %
Before nitration	0.7448	118.9	17.9
After nitration	0.7211	100.4	0

Aromatics by nitration, % = 17.6 Density or original crude = 0.823

$$\text{Toluene in original crude} = \frac{1066 \times 0.7448 \times 0.179 \times 100}{13000 \times 0.823} = 1.33\% \text{ (by weight)}$$

* δ^{20}_{g-e} *is the dispersion (11).*

Results

Preliminary experiments were performed in which feed rate, temperature, and catalyst composition were varied.

Variation of Feed Rate

Increasing the feed rate decreases the conversion very markedly (see Tables I and II). In the following tables, feed rates are given in cubic centimetres of liquid per hour per gram catalyst.

TABLE I

VARIATION OF FEED RATE. HEPTANE, PRACT. CATALYST NO. 2

Expt. No.	Temp., °C.	Feed rate, cc./gm. catalyst/hr.	Vol. gas, cc./gm. feed	Gas analysis, volume %					Aromatics, based on original feed, %
				CO_2	O_2	Unsaturates	H_2	CO	
19	475	0.72	180	0.6	0.8	0.3	88.5	0.8	5.2
20	475	0.27	356	0.2	1.5	0.2	83.5	0.1	9.5

Variation of Temperature

Increasing the temperature from 470° to 515° C. resulted in a considerable increase in conversion to aromatics (see Table III). A similar temperature effect may be noted in later tables (at higher temperatures the formation of coloured and gum producing products becomes pronounced).

TABLE II

VARIATION OF FEED RATE. HEPTANE, PURE. CATALYST NO. 4

Expt. No.	Temp., °C.	Feed rate, cc./gm. catalyst/hr.	Vol. gas, cc./gm. feed	Recovery, %	Aromatics based on original feed, %	Br No.
43	510	0.14	183	89.5	23.0	25.2
44	516	0.06	594	76.5	47.6	23.4

TABLE III

VARIATION OF TEMPERATURE AND CATALYST. FEED: HEPTANE, PRACT.

Expt. No.	Temp., °C.	Feed rate, cc./gm. catalyst/hr.	Vol. gas, cc./gm. feed	Gas analysis, volume %					Aromatics, based on original feed, %
				CO_2	O_2	Unsaturates	H_2	CO	
Catalyst No. 2									
29	470	0.27	133	0.2	1.5	0.2	83.5	0.1	9.5
10	500	0.29	—	0.0	0.4	3.8	74.9	1.5	18.4
27	515	0.27	274	0.2	0.1	0.5	90.5	0.1	21.7
Catalyst No. 3									
29	475	0.31	166	0.0	0.4	1.1	89.4	0.4	9.7
30	496	0.29	306	0.0	0.8	0.4	85.3	0.9	17.3
31	515	0.25	382	0.0	0.3	0.9	86.5	0.6	24.7
28	515	0.28	410	0.0	0.1	0.7	84.5	0.9	27.2

It should be remarked that the yield of 27.2% is equivalent to more than 60% conversion of the heptane actually present.

YIELD OF AROMATICS FROM TURNER VALLEY CRUDES BY CATALYTIC CONVERSION

In order to determine the possible yield of aromatics from Turner Valley crudes, catalytic conversion experiments were done on selected cuts from representative Turner Valley crudes. Typical results and calculations are recorded in Tables IV and V.

Effect of Recycling

Experiments in which the product was recycled over the catalyst are recorded in Table VI. In some experiments a small increase in yield of aromatics is indicated, but in others (Expts. 54 to 56) the yield falls off slightly. It appears that, using a catalyst containing 14% chromium trioxide (and the indicated feed rates), a maximum yield is obtained in one pass.

TABLE IV

CATALYTIC PRODUCTION OF AROMATICS FROM SELECTED CUTS FROM TURNER VALLEY CRUDES

Feed: Nitrated toluene cut No. IV. Catalyst No. 1

Origin of sample	Expt. No.	Temp., °C.	Feed rate, cc./gm. catalyst /hr.	Vol. gas, cc./gm. feed	Gas analysis, vol. %					Aromatics, based on original, %
					CO_2	O_2	Unsaturates	H_2	CO	
Royalite No. 45	9	510	0.28	300	0.1	0.7	1.2	83.6	0.5	18.6
Foothills No. 6	12	510	0.31	275	0.4	0.51	1.0	80.0	0.3	15.0
Foundation No. 1	13	510	0.24	330	0.0	0.2	0.8	84.1	0.5	18.8

TABLE V

YIELD OF AROMATICS (BY CONVERSION) FROM ORIGINAL CRUDE

	Royalite No. 45	Foothills No. 6	Foundation No. 1
Volume of crude, cc.	1000	1000	1000
Density of crude	0.8026	0.8193	0.7936
Wt. nitrated toluene cut, gm.	55.1	50.6	82.8
Aromatics from nitrated cut (see Table IV), %	18.6	15.0	18.8
Aromatics, based on crude, by conversion, %	$\frac{18.6 \times 55.1}{802.6} = 1.28$	$\frac{15 \times 50.6}{819.3} = 0.93$	$\frac{18.8 \times 82.8}{793.6} = 1.96$
Toluene, in original crude, %	1.52	1.34	2.05

TABLE VI

AROMATIZATION OF NITRATED TOLUENE CUT (V). TEMPERATURE, 515° C.

Expt.	Feed	State of catalyst	Feed rate, cc./hr. per gm. catalyst	Vol. gas, cc./gm. feed	Aromatics in products, %	Product, as % of feed	Br No.	Aromatics, based on crude, %
Calalyst No. 4								
45	Fresh V	*r**	0.16	326	35.1	84	16.3	2.13
46	Product of 45	*n.r.*†	0.14	277	49.8	85	21.3	2.57
47	Fresh V	*n.r.*	0.07	365	36.0	83	19.1	2.13
48	Fresh V	*r*	0.12	492	41.9	77.6	—	2.35
49	Prod. from 47	*n.r.*	0.14	322	46.4	87	26	2.42
50	Prod. from 49	*r*	0.14	290	60.4	81.5	19.6	2.57
51	Prod. from 50	*n.r.*	0.1	104	68.4	91	20.6	2.65
52	Prod. from 48	*n.r.*	0.17	84	50.3	95.4	20.2	2.69
53	Prod. from 46	*n.r.*	0.09	307	53.9	91	19.5	2.50
Catalyst No. 5								
54	Fresh V	*r*	0.28	385	50.1	75	19.7	2.72
55	Prod. from 54	*n.r.*	0.12	253	55.3	82	14.2	2.46
56	Prod. from 55	*r*	0.12	229	70.9	77	10.8	2.42

*r = Revivified.   †n.r. = Not revivified.

Since hydrocarbons such as the dimethylhexanes are present in the nitrated toluene cut, the products of catalytic aromatization will be expected to contain aromatics such as xylene, in addition to toluene.

Composition of Product

Sixty-five cubic centimetres of aromatized product (containing 56.8% aromatics) was fractionated in a small Podbielniak type column. The boiling point curve is recorded in Fig. 2 and indicates that the recovery of toluene from this fraction should not present any great difficulty.

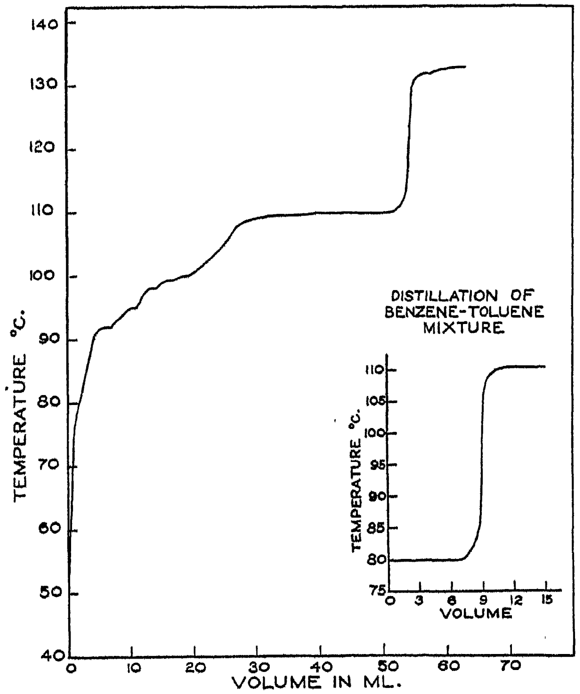

FIG. 2. *Distillation of aromatized cut (pressure, 760 mm.)*

The products of distillation were divided into three cuts: below 90°, 90° to 120°, and above 120° C., and the aromatics determined by dispersion. (The base value for the aromatized material was determined in the usual way and was found to be unchanged.) The results show that the aromatics are 5% benzene, 67% toluene, and 27% xylene. A duplicate experiment on 53 cc. aromatized product showed that the aromatics contained 66% toluene.

Discussion

The foregoing experiments indicate a maximum yield of aromatics of 2.72%, based on the original crude (see Table VI, Expt. 54). Since the aromatics contain 67% toluene the yield of toluene is 2.72 × 0.67 = 1.82%. The original crude contained 1.33% toluene, and thus the total recovery of toluene would be 3.15%. We may say that aromatization increases the yield of toluene by 137%. Under large-scale operating conditions the yield might possibly be slightly greater than this, since plant losses in handling and evaporation would probably be somewhat less than ours. Supposing a rating of 27,000 bbl. per day (289 lb. per bbl.), the possible recovery of toluene is $\frac{27{,}000 \times 289 \times 3.15\text{ lb.}}{100} = 250{,}000$ lb. per day for the whole of Turner Valley (1942). The optimum catalyst temperature is 515° C. Experiments using 14.2% chromium trioxide on alumina indicate that the maximum conversion is obtained with one pass over the catalyst. Using 9.7% chromium trioxide on alumina, the yield may be improved by two or three passes.

The optimum rate is approximately 6 gm. feed per hour using 65 gm. catalyst, and corresponds to a contact time of 73 sec. Assuming that the revivifying takes up about as much time as the conversion, about two tons of catalyst would be required per 1000 lb. toluene desired per day. The catalyst actually has quite a long life, but it is inadvisable to use it too long before revivifying since carbon is deposited. When much carbon is deposited, it becomes difficult to avoid overheating the catalyst, with consequent loss in activity, while burning off the carbon. It is suggested that the catalyst be revivified when an amount of feed equal to the weight of the catalyst has been passed over the catalyst.

Acknowledgments

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Note on the Preparation of 1-Methoxy-1,3-butadiene[1]

Recently a method has been described by Meier (2) for the preparation of 1-methoxy-1,3-butadiene by the pyrolysis of 1,1,3-trimethoxybutane over a catalyst of the approximate composition $BaO . 5SiO_2$. However, his description of the preparation of the catalyst is very incomplete and insufficient for the duplication of his results.

A preparation is now described that will produce a catalyst of composition varying from $BaO . 4SiO_2$ to $BaO . 5SiO_2$, with which conversion yields of 40 to 50% can be obtained consistently.

1-Methoxy-1,3-butadiene polymerizes to an appreciable extent on distillation. It could not be converted to a sulphone but it underwent the Diels–Alder reaction with maleic anhydride giving rise to 3-methoxy-1,2,3,6-tetrahydrophthalic anhydride. This last compound, when dehydrogenated, lost the methoxyl group and produced phthalic anhydride.

EXPERIMENTAL

Preparation of the Catalyst.—To a stirred solution of water glass (200 cc., sp. gr. 1.386) in water (500 cc.) was added dropwise a solution of barium nitrate (57.7 gm.) in warm water (500 cc.). Ammonium hydroxide (28%) was then added to the mixture and stirring continued for 20 hr. The resulting gel was collected on a large Büchner funnel, placed in a 4 litre beaker and dialyzed through a non-waterproofed commercial cellophane membrane with stirring and heating (3). The dialysis was continued (six hours) until a test for ammonia with Nessler's reagent was negative. The slurry was allowed to settle and, after decantation of the supernatant water, filtered with suction and dried in an oven at 110° C. Found: BaO, 37.44; SiO_2, 60.41%. Calc. for $BaO . 4SiO_2$: BaO, 38.96; SiO_2, 61.12%. Another batch of catalyst yielded the following figures: BaO, 34.86; SiO_2, 63.06%. The dried catalyst was broken into small pieces of about 0.5 cc.

1,1,3-Trimethoxybutane.—The material was prepared from crotonaldehyde as described by Meier (1). After careful fractionation through a Stedman column, 1,1,3-trimethoxybutane boiled at 55° C. (15 mm.) and 149° to 150° C. (747 mm.), d^{25} 0.916, n_D^{20} 1.4050. Molecular refractivity, found: 39.2; calc., 39.10. Calc. for $C_7H_{16}O_3$: C, 56.76; H, 10.81%; mol. wt. 148. Found: C, 57.57; H, 10.77%; mol. wt. (in benzene, cryosc.) 148.

1-Methoxy-1,3-butadiene.—The catalyst (a volume of about 100 cc.) is loaded into a vertical catalyst tube, 20 mm. inside diameter and 125 cc. capacity, which is inserted inside an electrically heated sleeve of 40 mm. outside diameter. The top part of the catalyst tube is filled with coarse pumice resting on top of the catalyst. The catalyst is activated by heating at 400° C. for 12 hr. in a stream of nitrogen. For operation, a feeding device is connected to the top of the catalyst tube while the lower end is connected to a condensation train cooled in dry-ice–acetone. The catalyst tube is heated, a stream of nitrogen is allowed to flow through the system and, when the required temperature has been reached, the trimethoxybutane is fed in at the desired rate. Trimethoxybutane is vaporized while going through the pumice and mixes with the nitrogen before it reaches the catalyst. The conditions finally adopted involved a temperature of 340° C., a nitrogen flow of 30 litres per hr. and a contact time* of 0.24, which is equivalent to a flow of trimethoxybutane of 0.4 cc. per sec. The catalyst gradually becomes poisoned and the yields decrease accordingly. The yields varied from 40 to 60%, but were most consistently between 40 and 50%.

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The product of the pyrolysis was washed with water and fractionated by rapid distillation. An azeotrope of methoxybutadiene and water, b.p. 67° C., was first obtained and then the methoxybutadiene, b.p. 89° to 90° C. Pure 1-methoxy-1,3-butadiene boils at 88° to 89° C. (772 mm.), d^{26} 0.830, n_D^{26} 1.4590. Mol. refractivity found, 27.1; calc., 27.4.

It is interesting to compare the similar constants of 2-methoxy-1,3-butadiene: b.p. 75° C. (745 mm.), n_D^{20} 1.4442, d^{20} 0.8281 (4).

3-Methoxy-1,2,3,6-tetrahydrophthalic Anhydride.—To a stirred solution of 1-methoxy-1,3-butadiene (12 gm.) in dioxane (25 cc.) cooled in an ice-bath was added slowly a solution of maleic anhydride (20 gm.) in dioxane (11 cc.). The reaction mixture was allowed to warm up to room temperature and stand for two hours. Addition of water caused the separation of an oil, which soon solidified. This was filtered, washed with water, and dried. Wt., 7.2 gm. It was found to consist of a large proportion of polymer. The product was digested with boiling benzene and the solution decanted from the insoluble polymer. The decantate was concentrated, allowed to cool, and diluted with petroleum ether. 3-Methoxy-1,2,3,6-tetrahydrophthalic anhydride crystallized out and, after one more crystallization from the same mixture, consisted of clusters of small, colourless, flat prisms, m.p. 99° to 100° C.† Wt., 1 gm. Calc. for $C_9H_{10}O_4$: C, 59.33; H, 5.49; OCH_3, 17.03%. Found: C, 59.12, 59.44; H, 5.57, 5.39; OCH_3, 16.72%.

Dehydrogenation of 3-Methoxy-1,2,3,6-tetrahydrophthalic Anhydride.—3-Methoxy-1,2,3,6-tetrahydrophthalic anhydride was heated with selenium for 30 min. at 325° to 350° C. in a stream of nitrogen, in a distilling flask, the side-arm of which was connected to a cooled receiver. An oil distilled which crystallized in the side-arm and the receiver. This was washed with methanol, the solution evaporated, and the residue fractionated *in vacuo*. A first fraction sublimed at 80° to 90° C. (0.3 mm.) and a second fraction sublimed at 160° to 180° C. (0.3 mm.). Fraction I separated from ether–petroleum-ether as colourless needles, m.p. 134° C., alone or in admixture with phthalic anhydride. The second fraction, crystallized from ethyl acetate, consisted of small, colourless prisms, m.p. 214° C. In admixture with phthalic acid (m.p. 215° C.) it melted at 214.5° C. Calc. for $C_8H_6O_4$: C, 57.83; H, 3.61%. Found: C, 57.76; H, 3.75%.

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* *The contact time was calculated as the volume of trimethoxybutane in cubic centimetres of liquid per volume of catalyst per hour.*

† *All melting points are corrected.*

Dehydrogenation by means of *n*-amyl disulphide (5), which does not involve as high a temperature, caused demethoxylation and gave rise to phthalic anhydride.

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THE INFLUENCE OF THE PHYSICAL PROPERTIES OF SODIUM SOAPS ON THEIR DISPERSIONS IN MINERAL OIL[1]

BY F. W. SOUTHAM[2] AND I. E. PUDDINGTON[2]

Abstract

The densities of the anhydrous sodium salts of the fatty acids from caproic to stearic have been measured over a temperature range of 30° to 300° C. and the results obtained correlated with the properties of lyophilic dispersions of sodium soaps in mineral oil.

Introduction

The conventional method of preparing stable lyophilic dispersions of saturated sodium soaps in mineral oils involves heating the soap, or the soap containing a limited amount of oil, to a temperature of about 160° C., and adding the remainder of the oil slowly and with constant stirring as the temperature of the dispersion is gradually reduced to 120° C. If the agitation is such that the system is subjected to high shearing stresses, the maximum temperature may then be reduced to about 120° C. and the total quantity of soap and oil may be treated at one time (2). Further reduction in the temperature, however, prior to the application of high shear produces an unstable dispersion in which the soap appears to be completely lyophobic. This sudden change from the lyophobic to the lyophilic system, which takes place within a short temperature interval, is of considerable interest, since a large density change in the soap occurs at about the same temperature, and could be associated with it.

Following the terminology of Thiessen (4, 5), who suggested "unidimensional melting" for the change in state that is found in a soap at the melting point of the corresponding fatty acid, bidimensional melting has been suggested as the cause of this second density change (1). Here, presumably, the soap crystal has absorbed enough thermal energy for the hydrocarbon chains to separate sufficiently for oil to penetrate the crystal lattice, and, at the same time, the soap becomes plastic. This penetration of oil is greatly assisted by shearing the crystal, and by the proper control of temperature and shearing forces, soap micelles of predetermined size, shape, and stability can be produced (2).

When the number of carbon atoms in the soap molecule has been reduced below eight, it is well known industrially that it is no longer possible to prepare

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Contribution from the Division of Chemistry, National Research Laboratories, Ottawa, Canada. Issued as N.R.C. No. 1503.

[2] *Chemist.*

stable dispersions by the conventional method. If the proposed explanation for the formation of the lyophilic soap micelles is correct, changes in state of the sodium soap crystal with temperature should show a discontinuity as the size of the molecule is reduced below eight carbon atoms. In view of this it was decided to investigate the density–temperature changes of the sodium soaps of the fatty acids on both sides of the critical eight carbon atom chain length. Results are reported from caproic to stearic.

Experimental

The stearic acid used in this work was laboratory prepared from a technical sample by the method of Philipson, Heldman, Lyon, and Vold (3) and had a melting point of 68.3° C. Palmitic, capric, and caproic acids were supplied by Eastman Kodak Co., myristic by City Chemical Corporation, and lauric and caprylic by the Paragon Testing Laboratories. The soaps were prepared by titrating an alcoholic solution of the acid with alcoholic sodium hydroxide, using phenolphthalein as an external indicator. The soap was then recovered by evaporation of the solvents.

In making the density determination, about 1.5 gm. of soap powder was melted *in vacuo* to remove the last traces of water and solvent. After cooling in an atmosphere of nitrogen, the cake of solid soap was removed and its density determined by a mercury displacement method.

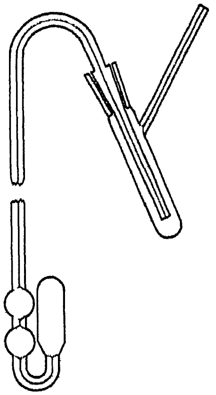

FIG. 1. *Form of dilatometer used.*

The dilatometers were of the form shown in Fig. 1 and were constructed and filled as follows. The soap block was placed in a sealed-off tube of slightly larger diameter, which was then drawn down and sealed to a 30 cm. length of capillary. The male member of a capillary bore ground glass joint, to which about 6 cm. of fine capillary had been sealed, was then attached, and the dilatometer completed by bending in the form shown in Fig. 1. Filling with mercury was accomplished by attaching the ground glass joint to a vacuum system and reducing the pressure to about 10^{-4} mm. of mercury, after which the mercury was forced into the dilatometer under atmospheric pressure.

The dilatometer bulbs were placed in an air thermostat, the temperature of which could be controlled to ± 0.2° C. A weighing bottle, containing sufficient mercury to cover the tip of the capillary, was then attached to the ground glass joint, and the mercury displaced from the dilatometer by the expanding soap could be determined precisely. A capillary vent in the weighing bottle prevented any loss of the mercury by evaporation during the experiments.

Results

Fig. 2 shows the results obtained with the soaps investigated. Increments of density rather than the absolute figures are shown on the graph in order to separate the curves. The actual densities found at 27.0° C. are given in Table I.

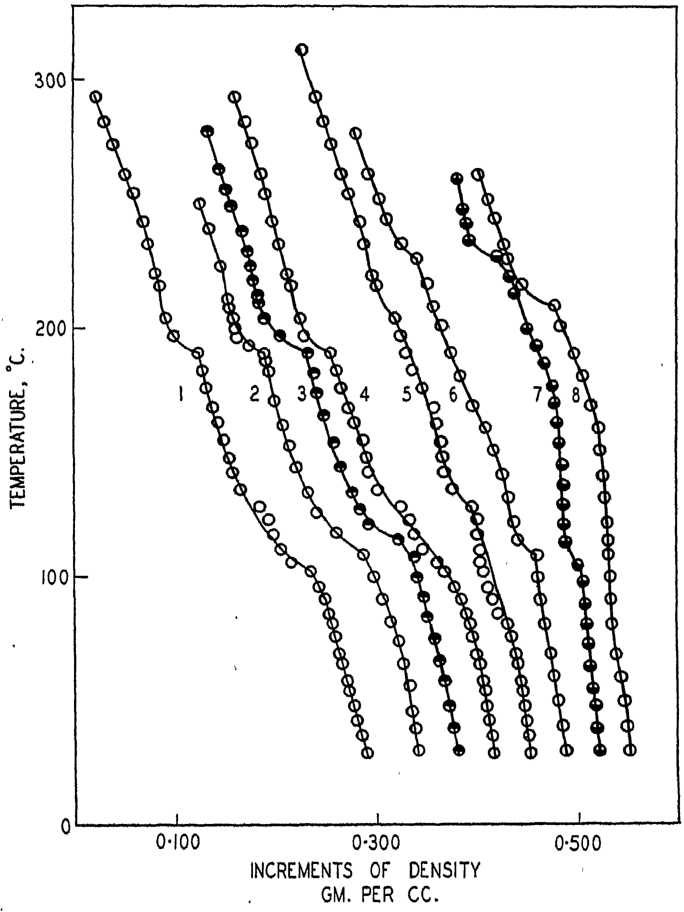

FIG. 2. *Density-temperature relations for anhydrous sodium soaps. Curves 1 to 8 represent respectively the relations for the sodium salts of stearic (technical), stearic, palmitic, myristic, lauric, capric, caprylic, and caproic acids.*

TABLE I

DENSITIES OF ANHYDROUS SODIUM SOAPS

Stearate, pure	1.103	Laurate	1.150
Stearate, technical	1.088	Caprate	1.172
Palmitate	1.111	Caprylate	1.214
Myristate	1.133	Caproate	1.264

The curves shown are in substantial agreement with the qualitative data presented by Vold, Macomber, and Vold (6), and the usual large changes in density are shown at 100° to 120°, and 190° C. in the case of the higher molecular weight fatty acids, the latter density break occurring at higher temperatures as the chain length of the fatty acid is reduced. No substantial difference can be noted between the samples of pure and technical grades of sodium stearate. The bidimensional melting point, which is shown by all the soaps down to and including sodium caprylate, is entirely absent in the case of the caproate. The rather large increase in density in this vicinity indicated by Vold and co-workers (6) for the caprate was not found; its behaviour appeared to be in line with that of the higher members of the series.

The absence of bidimensional melting in sodium caproate suggests that the non-polar bonds between the adjacent hydrocarbon chains become approximately as strong as the polar bonds between the sodium carboxyl groups when the carbon chain length is sufficiently reduced, and only one melting point will occur. This is borne out by the fact that only one break is found in the density curve, at 210° C., for the soap containing six carbon atoms. The theory that the formation of lyophilic dispersions of sodium soaps in mineral oil by a comminution process is dependent on the existence of bidimensional melting in the anhydrous soap is thus in agreement with the experimental facts, since only those soaps possessing it are capable of forming stable dispersions.

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THE FLOW PROPERTIES OF SOME ANHYDROUS SODIUM SOAPS[1]

By F. W. Southam[2] and I. E. Puddington[2]

Abstract

The flow properties of anhydrous sodium stearate have been followed in some detail over the temperature range 45° to 140° C., using an extrusion plastometer. Comparative results have been obtained at a single temperature with the sodium soaps of some of the lower fatty acids. The results indicate large changes in the properties of sodium stearate at 68° and 105° C. An abrupt change is also observed when the number of carbon atoms in the soap is reduced below eight.

Introduction

Previous publications have demonstrated several changes of state in the sodium soaps of the higher fatty acids as they are heated from room temperature to the melting point. For example, dilatometric measurements over this temperature range show two gross irregularities in the density–temperature curve at about 105° to 120° C. and 200° C., with minor breaks at other temperatures (1, 3, 6).

A change in the state of dispersion of aqueous soap solutions at the melting point of the fatty acid used in preparing the soap, noted years ago by Kraft, formed the subject for several papers by Thiessen and co-workers (4, 5). They noted irregularities in the specific volume, dielectric constant, optical double refraction, and specific heats of the soaps at this temperature, as well as a broadening in the interference representing the larger spacing at right angles to the axis of the soap crystal. From the changes so observed, Thiessen concluded that the soap underwent partial melting at this point; that is, sufficient thermal energy had been provided to bring about a loosening of the crystal lattice in one dimension. A similar explanation has been suggested to account for the larger density change at 105° to 120° C. (1). If these postulates are correct, the flow properties of the soaps should show marked changes at these points, and an investigation into this phase of their behaviour might be expected to make worth while contributions to our knowledge of the nature of soaps.

When a solid material is completely melted, the changes in its flow properties are too great to be conveniently followed by means of a single instrument, and the material for the present paper is confined to the results obtained in a preliminary investigation of several soaps in the temperature range of 45° to 140° C.

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[1] *Manuscript received October 28, 1946.*

Contribution from the Division of Chemistry, National Research Laboratories, Ottawa, Canada. Issued as N.R.C. No. 1508.

[2] *Chemist.*

Experimental

The soap samples used were a part of those employed in another investigation; their preparation and properties have been described (3). Changes in flow properties were followed with an extrusion plastometer similar to the one described by Gallay and Tapp (2). The extrusion capillary was 0.0109 cm. in diameter and 0.66 cm. in length. Pressure was applied to the plastometer with a manually controlled, 10 ton, Carver laboratory press. The pressure was measured by means of a special gauge inserted between the plastometer and the top platen of the press. It consisted of a lapped piston and cylinder, of 0.5 sq. in. cross-sectional area, filled with S.A.E. No. 60 oil; an indicating pressure gauge was coupled directly to the oil chamber. The gauge was calibrated with known weights before use. Pressures on the soap could be maintained within ± 33 lb. per sq. in. The temperature of the plastometer was controlled to ± 0.5° C. with an air thermostat.

Soap blocks, previously melted *in vacuo* to remove traces of water, were moulded to the correct size before inserting into the plastometer. One and one-half hours was allowed for the temperature of the sample to reach equilibrium before readings were taken, and several feet of the soap were extruded

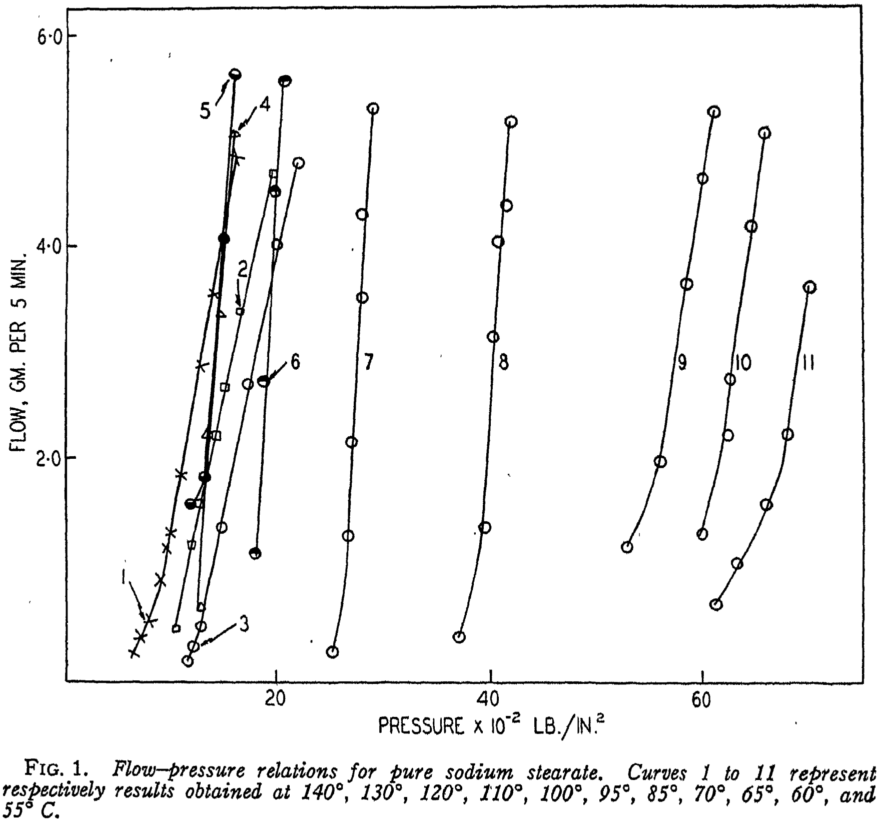

FIG. 1. *Flow-pressure relations for pure sodium stearate. Curves 1 to 11 represent respectively results obtained at 140°, 130°, 120°, 110°, 100°, 95°, 85°, 70°, 65°, 60°, and 55° C.*

before the thread was cut off flush with the capillary, and the amount flowing in five minutes noted by weighing.

Results

Fig. 1 shows the behaviour of pure sodium stearate when the rates of flow at various pressures are observed over a temperature range. Fig. 2, included for comparison, shows similar results for technical sodium stearate.

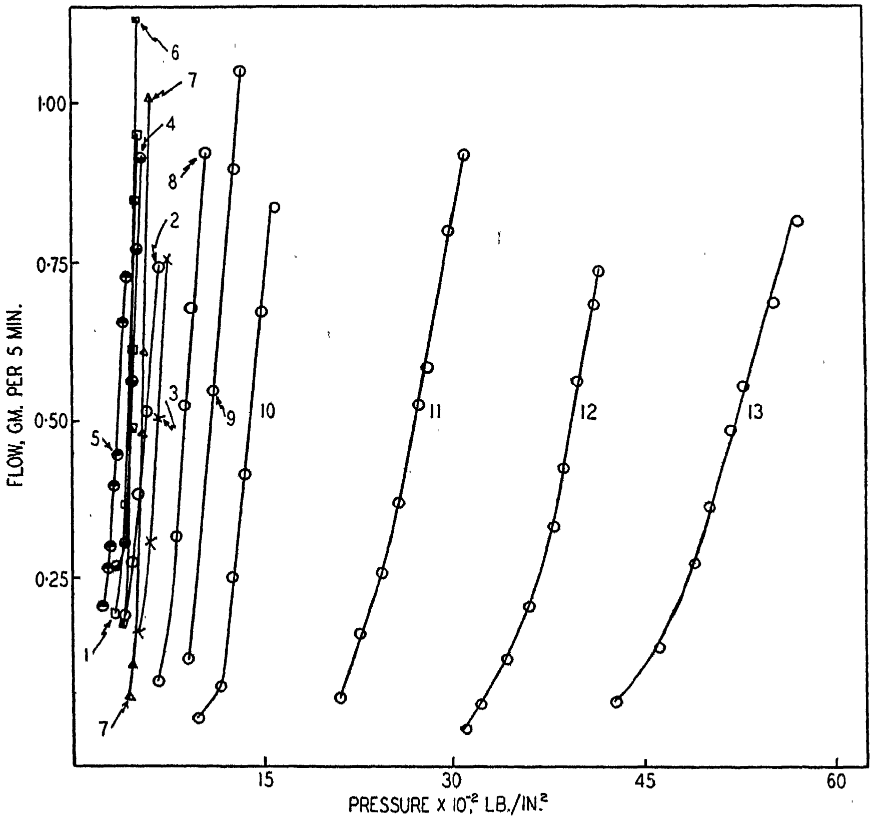

FIG. 2. *Flow-pressure relations for technical sodium stearate. Curves 1 to 13 represent respectively results obtained at 140°, 130°, 125°, 115°, 110°, 100°, 90°, 75°, 65°, 60°, 55°, 50°, and 45° C.*

In the case of the pure soap, large changes in the slopes of the curves may be noted between 100° and 110° C. and between 65° and 70° C., while the deviations in the curves representing the technical soap are at somewhat different temperatures and are not so pronounced. This is not surprising since the technical material contains a mixture of fatty acids (m.p., 52° to 55° C. compared to 68.5° C. for pure stearic), which would be expected to mask the behaviour of a single pure acid.

Figs. 3 and 4 supplement Figs. 1 and 2 and show respectively the variation of mobility and yield value (the extrapolated intercept of the pressure axis at zero flow) with temperature. These graphs accentuate the discontinuities noted in Figs. 1 and 2, both showing marked breaks at the melting point of the fatty acid and in the vicinity of 110° C.

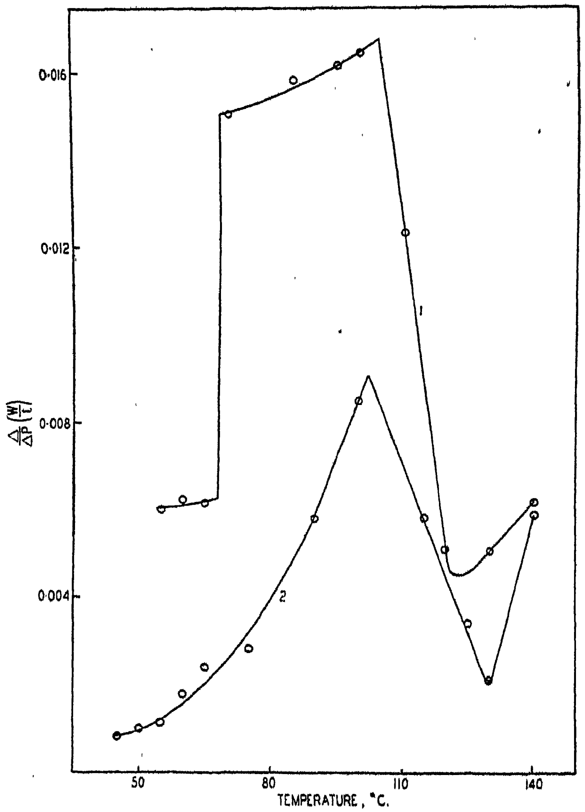

FIG. 3. *Change in mobility with temperature. 1, pure sodium stearate; 2, technical sodium stearate.*

It should be noted here that the pressure figures quoted are not corrected and are therefore not independent of the capillary dimensions. Rates of flow have also been reported as masses rather than volumes. The irregularities noted in the flow properties, however, are so large that the change in units has little effect on the general shape of the curves.

In Fig. 5 the change in yield value per carbon atom is plotted against the number of carbon atoms in the molecule. The marked increase in yield value as the number of carbon atoms is reduced from eight to six is obvious. These values were obtained from flow–pressure curves of the different soaps at 140° C.

A few experiments, carried out without melting the soap *in vacuo* to ensure the complete removal of water, indicated that traces of moisture had little effect on the flow properties below 100° C.; above this temperature the effect was to increase the rate of flow at any pressure.

Discussion

Thiessen's postulate, that the soap undergoes partial melting at the melting point of the fatty acid from which it is prepared, appears to receive support from the present work, since a marked decrease in yield value and a tremendous increase in mobility occur at this point. Both of these changes would be expected with the loosening of the crystal bonds in one dimension and the consequent provision of easier slip planes. Qualitatively, a change was noted in the appearance of the extruded soap; below 68° C. it tended to crumble easily, while above this point it was much more coherent.

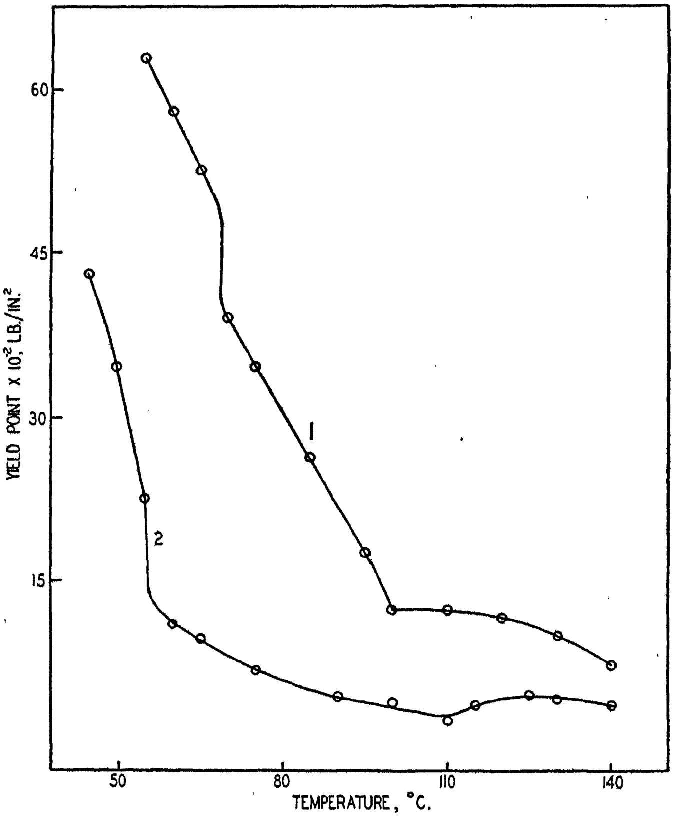

FIG. 4. *Change in yield value with temperature. 1, pure sodium stearate; 2, technical sodium stearate.*

As the temperature is increased over a further 40° C. interval, the yield value continues to fall in a linear manner. This thermal weakening of the soap crystal continues until a temperature of about 105° C. is reached; after which the yield value falls off at a greatly reduced rate over the remaining temperature interval examined. This point, 105° C., would appear to indicate complete disruption of another crystal bond which had a strength not greatly different from that broken at 68° C., since the rates of falling-off in the yield point with increased temperature were virtually identical above and below the unidimensional melting point. The much more gradual falling-off in yield point above 105° C. indicates much stronger remaining crystal forces. Since the soap molecule is distinctly heteropolar, much stronger bonds exist between the highly polar sodium carboxylic groups than between the non-polar hydrocarbon chains in the crystal lattice, and such behaviour is not unexpected. The behaviour of the technical sample is essentially the same as that of the pure soap, due allowance being made for its heterogeneous nature.

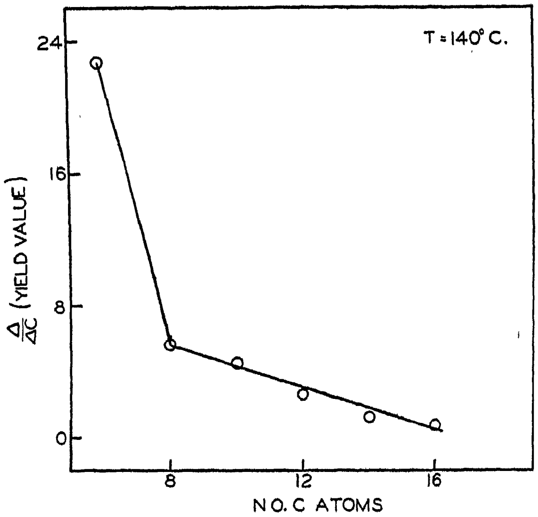

FIG. 5. *Rate of change of yield value with the number of carbon atoms in pure sodium soaps.*

An alternative explanation might be based on the findings of Vold *et al.* (6), who reported the appearance of new soap phases at 90°, 117°, and 132° C. Since only one substantial change in flow properties has been found, however, that does not coincide with any of the temperatures noted by Vold, such an explanation does not appear to be valid.

Changes in the mobility of the soap with temperature, shown in Fig. 4, are also of considerable interest. In the temperature intervals 45° to 65° C. and 70° to 100° C. the mobility is approximately constant with the expected large increase in the 65° to 70° C. range. The large and abrupt fall at 105° C. followed by a slight rise is somewhat unexpected. However, this can be explained on the basis of the following considerations. When the soap crystal has undergone unidimensional melting, slip planes are afforded that offer little resistance to flow once the yield value has been exceeded. When the second set of crystal bonds are broken, however, considerable resistance to flow is set up by the interference of the long molecular chains, and more work will have to be done to push them past each other than before the bidimensional melting. That this is the case may be seen on a macroscale. Below 110° C. the soap is quite brittle while at higher temperatures it is rather plastic and can be drawn out into long fibres. This increased cohesion and fibre forming property are doubtless due to the mutual interference of groups of molecules. The gradual weakening of the remaining crystal lattice forces will account for the slow increase in mobility after the initial large decrease.

Fig. 5 indicates the increasing strength of the non-polar crystal bonds as the hydrocarbon chain is shortened. The decided increase in the rate of change of yield point per carbon atom between eight and six carbon atoms shows a very marked increase in bond strength in this region. This is in perfect agreement with dilatometric results, where it was found that, while a soap with eight carbon atoms showed the usual large break in the density–temperature curve, indicating bidimensional melting, this portion of the curve was completely linear in the case of the soap containing six carbon atoms. It also bears out the observations of grease makers, that it is not possible to prepare greases in the usual way using soda soaps containing fewer than eight carbon atoms.

Acknowledgment

The valuable technical assistance rendered by R. Farnand and R. Schnarr during the course of this work is gratefully acknowledged.

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A NOTE ON THE USE OF MULTI-TIP ELECTRODES IN POLAROGRAPHIC WORK[1]

By J. McGilvery,[2] R. C. Hawkings,[3] and H. G. Thode[4]

Abstract

In the past, a dropping mercury electrode for polarographic work has consisted of a single capillary dipping in a solution. We have used two or more capillaries in parallel to increase cathode surface and thereby increase the diffusion current and the sensitivity of the instrument. The results indicate that each tip gives a diffusion current proportional to its calibration constant and that multi-tip electrodes give diffusion currents proportional to the sum of the capillary constants. Further, galvanometer oscillations are reduced considerably by the use of multi-tip electrodes. The use of multi-tip electrodes, therefore, makes it possible to extend the limits of detection and provides a means for reducing objectionable galvanometer oscillations.

During the war, polarographic procedures were developed for the determination of trace elements in metals and alloys (1, 2). In the course of this work, a capillary was found with two parallel bores. This chance use of a double-tip electrode led to a general study of multi-tip electrodes, with the view of extending the detection limits of the polarograph and improving on its accuracy. It was found that each tip gave a diffusion current proportional to its calibration constant, and that a five-tip electrode gave a diffusion current proportional to the sum of the five capillary constants. In view of the need for more sensitive analytical methods, it seemed desirable to report briefly on our use of multi-tip electrodes.

The average diffusion current during the life of a mercury drop is given by the 'Ilkovic equation', which can be expressed as follows:

$$_{av}i = 605\ n\ D^{1/2}\ C\ m^{2/3}\ t^{1/6}\ ,$$

where n is the number of faradays of electricity required per mole of electrode reaction,

D is the diffusion coefficient in units cm.^{2} sec.$^{-1}$,

C is the concentration of the reducible material in terms of moles per cc.,

m is the rate of flow of mercury from the capillary in gm. sec.$^{-1}$, and

t is the drop time of the capillary in sec.

The factors determining the magnitude of the diffusion current may be separated into two main groups: those dependent on the solution n, D, and C, and those inherent in the apparatus, m and t. The use of multi-tip electrodes makes it possible to increase the factor $m^{2/3}\ t^{1/6}$ and still have t of suitable magnitude for polarographic work. The method is simply to connect two or more capillaries in parallel with the mercury drops from each flowing into the same solution. In this way, each capillary or tip acts as a separate cathode, and each should give rise to a diffusion current proportional to its $m^{2/3}t^{1/6}$ factor. The total diffusion current should, therefore, be proportional to the sum of these factors for the different tips.

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[1] *Manuscript received January 6, 1947.*
Contribution from McMaster University, Hamilton, Ont.

[2] *Senior student; now with Polymer Corporation, Sarnia, Ont.*

[3] *Graduate student; now at Northwestern University, Evanston, Ill., U.S.A.*

[4] *Professor of Chemistry.*

The results reported below were obtained with a Sargent Model XI Polarograph using penta-tip electrodes.

Results and Discussion

Fig. 1 shows typical Cd^{++} waves obtained with a 5×10^{-6} molar solution of cadmium nitrate. The average height of the Cd^{++} waves was found to be 8.6 ± 0.3 cm. for the six curves reproduced on a reduced scale in Fig. 1. Actually, the average wave height obtained for a large number of determinations made with three different test solutions is in agreement with this value.

The $m^{2/3}t^{1/6}$ factor was determined for each of the five capillaries used in the penta-tip electrode. The sum of these factors for the five capillaries was found to be 16.2 mgm.$^{2/3}$ sec.$^{1/2}$. Substitution of this value in the 'Ilkovic equation' gives an average diffusion current of 0.264 μamp. for the above solution (5×10^{-6} *M* cadmium nitrate) or an equivalent wave height of 8.8 cm. This is in good agreement with the wave height found.

The results of determinations made with cadmium nitrate solutions ranging in concentration from 5×10^{-6} to 1×10^{-7} using a penta-tip electrode are given in Table I.

TABLE I

Cd^{++} WAVES OBTAINED WITH PENTA-TIP ELECTRODE

Supporting electrolyte: 0.1 molar potassium chloride; 0.1% gelatin. Temp., 25° C.

Concentration of $Cd(NO_3)_2$ solution, moles/litre	Wave height, cm.	Ratio of wave height to concentration
5×10^{-6}	10.4	2.7×10^6
1×10^{-6}	2.7	2.1×10^6
7.5×10^{-7}	2.7	3.6×10^6
5×10^{-7}	2.1	4.2×10^6
1×10^{-7}	No wave	

Because of high residual currents, it was not possible to detect the Cd^{++} wave for the 10^{-7} *M* cadmium nitrate solution. However, it may be possible to overcome this difficulty by using suitable compensating resistances and perhaps by lowering the pressure head of mercury and thereby increasing drop time.

Finally, it was found that galvanometer oscillations are reduced considerably by the use of multi-tip electrodes. Since the drops falling from the different tips are out of phase, these unwanted oscillations, which are most serious when operating at high sensitivity, are considerably reduced. The same effect has been achieved by condenser damping (3, pp. 231-233). However, with the multi-tips there is the added advantage of increased sensitivity.

The use of multi-tip electrodes, therefore, makes it possible to extend the limits of detection by the polarographic method, and provides a means for reducing objectionable galvanometer oscillations.

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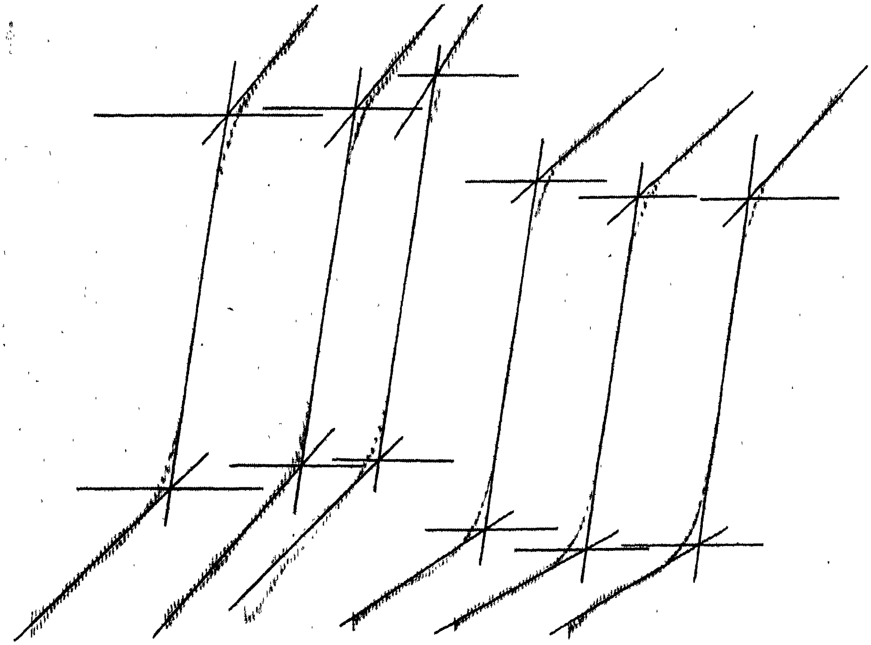

FIG. 1. *Typical Cd^{++} waves obtained for a 5×10^{-6} M solution using a penta-tip electrode.*

THE THERMAL DECOMPOSITION OF HYDROGEN PEROXIDE VAPOUR. II.[1]

By Paul A. Giguère[2]

Abstract

The decomposition of hydrogen peroxide vapour has been investigated at low pressures (5 to 6 mm.) in the temperature range 50° to 420° C., for the purpose of determining the effect of the nature and treatment of the active surfaces. The reaction was followed in an all-glass apparatus and, except in one case, with one-litre round flasks as reaction vessels. Soft glass, Pyrex, quartz, and metallized surfaces variously treated were used. In most cases the decomposition was found to be mainly of the first order but the rates varied markedly from one vessel to another, even with vessels made of the same type of glass. On a quartz surface the decomposition was preceded by an induction period at low temperatures. Fusing the glass vessels slowed the reaction considerably and increased its apparent activation energy; this effect was destroyed by acid washing. Attempts to poison the surface with hydrocyanic acid gave no noticeable result. The marked importance of surface effects at all temperatures is considered as an indication that the reaction was predominantly heterogeneous under the prevailing conditions. Values ranging from 8 to 20 kcal. were found for the apparent energy of activation. It is concluded that the decomposition of hydrogen peroxide vapour is not very specific as far as the nature of the catalyst is concerned.

In the first part of this investigation (2) Baker and Ouellet studied the thermal decomposition of hydrogen peroxide vapour on Pyrex in the range 70° to 200° C. with special emphasis on the effect of the shape and size of the reaction vessels. A few trial runs with soda-glass and fused Pyrex vessels indicated that the nature as well as the ultimate treatment of the active surface were important factors in determining the rate of the reaction. Therefore it was felt desirable to extend their work in that direction. An all-glass apparatus was used in order to avoid any contamination of the surface. This also permitted the reaction to be followed at higher temperatures. More than 300 runs were made, the results of which are summarized below.

Experimental

The reaction vessel, in most cases a one-litre round flask *A* (Fig. 1), was placed in a thermostat made either of an oil-bath or, at temperatures above 200° C., of an electric furnace. In both cases the temperature was kept constant to ± 0.3° C. by means of a mercury regulator or a resistance thermometer and an electronic relay (18). The temperature was measured with a mercury thermometer or a calibrated thermocouple. The reaction vessel could be connected either to the vacuum pump or to the source of hydrogen peroxide, *C*, through a special stopcock of the mercury-seal type, *D*. At first this stopcock was lubricated with only a little graphite to prevent introducing any volatile material into the reaction system. Later on some Apiezon

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[1] *Manuscript received October 10, 1946.*

Contribution from the Department of Chemistry, Laval University, Quebec, Que. Presented at the Canadian Chemical Conference, Toronto, June 1946.

[2] *Assistant Professor of Physical Chemistry.*

M grease was used without any ill-effect. All the tubing containing hydrogen peroxide vapour was heated to 40° C. with a nichrome winding wrapped in asbestos. In order to fill or evacuate the whole system quickly the connecting tubes were made rather large, 8 mm. in diameter. The pressure was measured directly on a Bourdon gauge, *B*, by means of a measuring microscope reading to 0.01 mm. Preliminary calibration against a Dubrovin mercury manometer had shown that the deflection of the gauge was strictly proportional to the pressure differential over a region much wider than that normally used. Two of these gauges were used in succession, the first one (up to Run 264) having a sensitivity of 2.9, and the second one, of 3.7 mm. of mercury per mm. of deflection. To dampen the vibrations the tip of the glass pointer was immersed in Apiezon oil, the vapour pressure of which was so low that it had no appreciable effect on the zero point of the gauge. This was tested frequently and usually was found to remain unchanged over a period of many days. A coiled heater was placed around the upper part of the gauge to prevent condensation of the vapours.

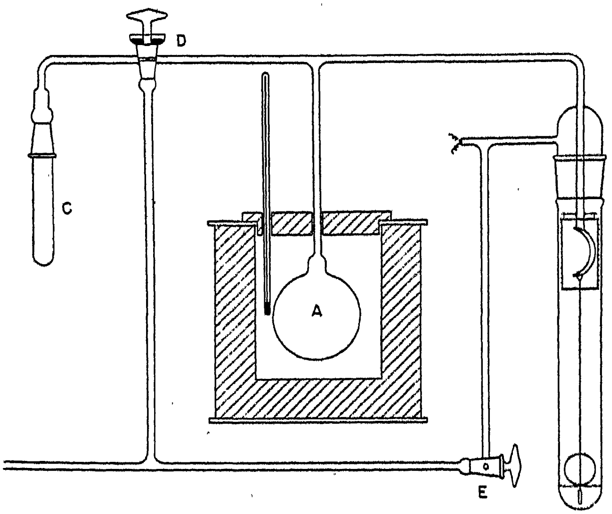

FIG. 1. *Apparatus used in following the decomposition of hydrogen peroxide vapour.*

The hydrogen peroxide used was prepared by fractional distillation of a 30% commercial solution. Its concentration was of the order of 95 to 99%; no special care was taken to keep it constant, as the rate of decomposition was known to be independent of the original composition of the vapour (2). It must be mentioned at this point that the vapour contained in the reaction vessel was not in equilibrium, strictly speaking, with the liquid in tube *C* because the two were separated by a length of tubing (in the present case, 60 cm.) that acted as a fractionating column. Since hydrogen peroxide is somewhat less volatile than water this fractionation effect through a narrow tube was not negligible. Therefore the composition of the vapour could not be calculated accurately from partial pressure data (8). Before starting a run the reaction vessel was evacuated to 0.01 mm. of mercury or better by means of an oil pump. The tube containing the liquid hydrogen peroxide was quickly evacuated and then heated to about 37° C. by immersing in a water-bath. The vapour was then admitted into the reaction system through stopcock *D*. This took usually 10 to 15 sec., after which the rate of the reaction was measured. When enough time had elapsed to take the 'infinity' reading the entire system was evacuated again for another run. In order to avoid introduction of dust particles, air was never admitted into the apparatus during a series of runs. The pressure of the vapour at the beginning of a reaction was of the order of 5 mm. and it never varied much from that value.

Results

Except in a few odd cases mentioned later the results were found to fit the first order equation:

$$k = \frac{2.303}{t} \log \frac{a}{a - x},$$

at least until the reaction was about 90% completed. Towards the end there was a tendency for the reactions, specially the more rapid ones, to slow down somewhat. This effect may be attributed partly to the diffusion into the reaction vessel of the peroxide vapour contained in the connecting tubes, which amounted to 12 to 15% of the total. The reactions in any given series were run as closely as possible to one another and scattered with respect to temperature in order to detect any ageing of the glass surface. The run number is given in each case to indicate the order in which they were carried out. As a rule any given reaction could be duplicated fairly exactly provided the necessary precautions were taken to avoid the slightest alteration of the active surface. The curves in Fig. 2 give an idea of the average degree of reproducibility of two consecutive reactions. In all cases the pressures given are readings of the measuring microscope.

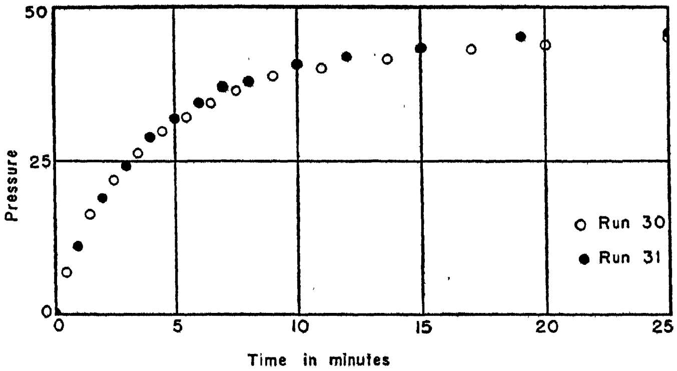

FIG. 2. *Decomposition curves for two consecutive reactions in vessel I at 200.8° C.*

I. DECOMPOSITION ON PYREX

Reaction Vessel I

The apparatus was first tried out with a Pyrex flask that had been thoroughly cleaned and fused. The regular procedure adopted for the present investigation consisted in cleaning the glass for five minutes with a warm chromic acid solution, rinsing repeatedly with distilled water and finally with redistilled water (conductivity less than 0.1 p.p.m. as sodium chloride). Steaming the flask had the same effect as the final rinsing. Fusing was done by heating, while rotating the flask slowly, in the flame of two Méker burners until the entire surface had been brought in turn to the softening point. This operation took over an hour but very little distortion of the flask ensued. Because of some defect in the apparatus the first 25 runs had to be discarded. Before the necessary alterations could be made, six months had elapsed and, as was found later, the effect of fusing the glass had partially disappeared by then. However, the results obtained under these conditions are reported here (Fig. 3 and Table I) as an example. In order to save space, only the rate constant, obtained graphically, is given for each run. The apparent energy of activation E was obtained from a plot of log k vs $1/T$.

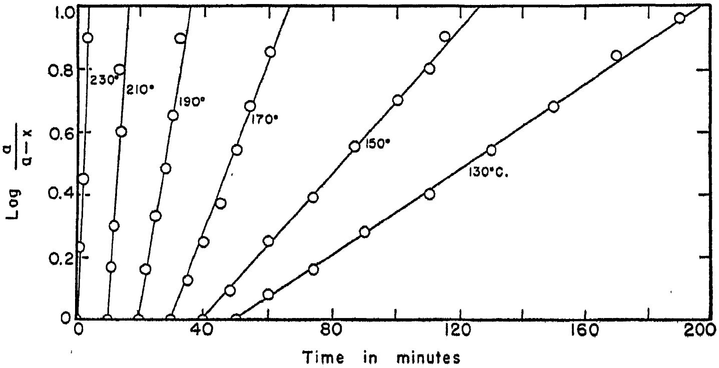

FIG. 3. *Decomposition in reaction vessel I between 130° and 230° C. The curves are shifted along the time axis to avoid confusion.*

Reaction Vessel II

The rates observed with the first vessel were higher than those found by Baker and Ouellet for a fused Pyrex surface. To afford some means of comparison the flask they used (their vessel *H*) was cleaned and fused anew. The activity of the surface was thus very much decreased so that it was possible to follow the reaction up to 375° C. While making these runs the following phenomenon was observed by accident. If the reaction vessel was filled as usual and then most of the hydrogen peroxide vapour pumped out quickly before it had time to decompose appreciably, then on further filling the vessel the reaction seemed to be of zero order until about three-quarters complete (Run 52, Fig. 4). Furthermore the final pressure reading was greater than in a normal run by as much as 50% in some cases, very likely

TABLE I

DECOMPOSITION IN PYREX VESSELS

Run No.	T,° C.	$k \times 10^3$/sec.	Run No.	T,° C.	$k \times 10^3$/sec.
Reaction Vessel I					
37	129.2	0.19	29	181.4	1.65
39	138.6	0.28	31	200.8	3.6
28	159.7	0.78	40	220.5	6.4
35	170.2	1.15	41	231.0	8.6
	E = 15.5 kcal./mole				
Reaction Vessel II					
171	205	0.12	173	300	3.3_8
181	225	0.39	177	325	7.4_3
180	250	0.9_6	174	350	12.3
179	275	2.2_2	175	375	22.2
	E = 18.2 kcal./mole				

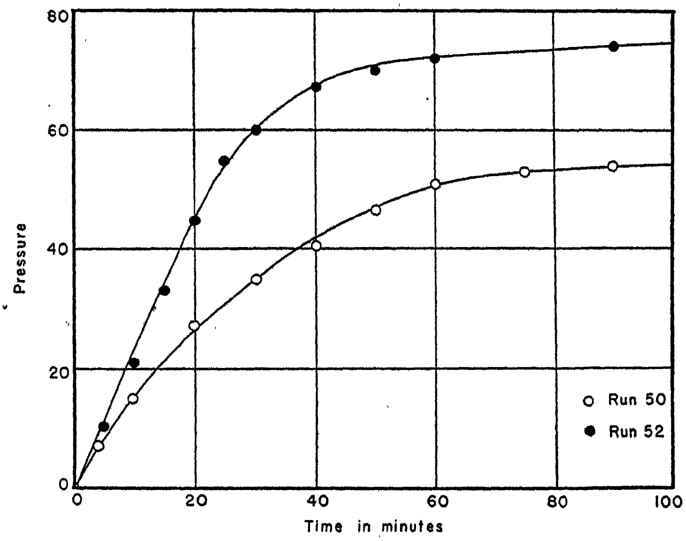

FIG. 4. *Decomposition curves for a Pyrex reaction vessel at 183° C. showing the effect of adsorption due to repeated filling (Run 52).*

owing to a corresponding increase in the amount of hydrogen peroxide present in the reaction vessel. It was possible to duplicate this result fairly closely by repeating the same operations. Similarly the behavior of the reaction vessel reverted to normal upon regular operation. The significance of these observations will be discussed below.

Reaction Vessel III

The above results proved conclusively that two vessels, even if made of the same material, can give widely different rates of decomposition and activation energies. The next series of runs were made to show the effect

TABLE II

DECOMPOSITION IN REACTION VESSEL III

Run No.	T, ° C.	$k \times 10^3$/sec.	E, kcal./mole
137	140	1.10	12.6
147	164	3.07	
146	185	5.04	
145	205	9.6	
144	224	15.1	
139	245	25.5	
Fused			
250	240	0.97	18.7
248	260	2.02	
251	289	4.2	
249	305	7.7	
Treated with chromic acid			
257	98	0.48	7.8
255	140	1.45	
253	210	5.7	
Fused again			
261	222	1.77	15.8
260	288	11.6	
Washed with hot water			
265	139	0.52	16.1
262	157	1.08	
266	175	2.54	
Coated with salt (Na_3PO_4)			
270	59	0.77	21.6
272	93	11.8	
269	103	35	
Etched with hydrofluoric acid			
281	130	0.33	8.4
282	148	0.48	
278	162	0.72	
283	225	2.43	

of various treatments on a given reaction vessel. The results observed are summarized in Table II. Fusing a glass (Pyrex) surface reduced its activity by a factor of about 20, while the temperature coefficient of the decomposition increased markedly. This effect was destroyed by cleaning the vessel with hot chromic acid. By repeating these operations the glass surface could be restored to nearly the same activity at least a few times. As could be expected with an heterogeneous reaction, the rate was increased considerably by coating the vessel with a salt. This was done by washing the flask with a saturated solution of trisodium phosphate and draining. Harris (9) has observed a similar phenomenon in the decomposition of hydrogen ethyl peroxide. Etching the glass surface with aqueous hydrofluoric acid also increased its activity, though not as much as was anticipated. After this treatment, however, the reaction became erratic, so that the rates and the temperature coefficient given are not reliable. Extrapolation shows that throughout the above series of treatments it was possible to vary the rate of decomposition by a factor of the order of 10^5.

Reaction Vessel IV

An attempt was made to run the reaction at a temperature as high as feasible in order to detect the possible existence of any homogeneous decomposition of the peroxide vapour. Although no relation between reaction velocity and surface to volume ratio of the vessel has been found (2) because of the difficulty of getting standardized surfaces, it was logical to use a large vessel for this purpose. Out of a number of two-litre flasks taken from the stock available, one was chosen that had a relatively low activity so that the reaction could be followed up to 420° C. (Table III). Yet throughout this interval of more than 260° C. the temperature coefficient of the reaction remained essentially constant.

TABLE III

REACTIONS IN A TWO LITRE PYREX VESSEL (IV)

Run No.	T,° C.	$k \times 10^3$/sec.	Run No.	T,° C.	$k \times 10^3$/sec.
236	156	0.19	240	324	8.5
237	196	0.96	241	372	10.3
238	228	2.43	235	392	12.5
231	257	2.31	242	419	18.0
239	271	5.1	243	419	19.1

$E = 7.5 - 8.0$ kcal./mole

II. DECOMPOSITION ON SOFT GLASS

Reaction Vessels V and VI

It is well known that solutions of hydrogen peroxide decompose more rapidly in soda-glass containers than in Pyrex. This has been generally attributed to the slow solution of the alkaline constituents of the glass that promote the decomposition of the peroxide. Baker and Ouellet had made a few trial runs with a soft-glass vessel that proved to be very active even at low temperatures. However, the flask they used was old and nothing was known of the composition of the glass itself. The experiments reported here were carried out in soda-lime flasks made specially for this purpose and kindly supplied by the Kimble Glass Co. The first one used was connected to the reaction system through a ground-glass joint held together with a little Apiezon *W* wax. After about 20 normal runs (Nos. 58 to 78) the reactions became erratic and finally were of purely zero order. A second flask connected similarly showed the same phenomenon. Upon investigation it was discovered that a trace of the Apiezon wax had crept inside the glass joint, and, since this wax decomposed hydrogen peroxide violently, it created an active spot. Diffusion of the reagent and products to and from this spot resulted in an apparent zero-order reaction. On replacing the ground joint by a graded seal, the decomposition became normal again. As can be seen from the results in Table IV, the rates of the reaction were markedly different in the two flasks although the flasks were of the same make and subjected to identical treatments. A few runs were tried in vessel V previously evacuated down to 10^{-4} mm. of mercury by means of an oil diffusion pump and a liquid-air trap. As a result the reaction was slowed down to about half its normal value but the temperature coefficient remained unchanged (Table IV). Above

TABLE IV

REACTIONS IN SOFT GLASS VESSELS (KIMBLE'S STANDARD FLINT GLASS)

Run No.	T,° C.	$k \times 10^3$/sec.	Run No.	T,° C.	$k \times 10^3$/sec.
Reaction Vessel V					
58	50.0	0.12_5	After pumping down to 10^{-4} mm. Hg		
59	70.3	0.27_5	61	89.3	0.48
60	89.3	0.72	68	128.5	2.0_2
62	108.6	1.87	76	139.0	2.3_5
69	128.5	3.8	75	159.5	10.4
77	139.0	5.7			
67	147.7	7.7			
74	159.5	18			
	E = 11.3 kcal./mole			E = 11.5 kcal./mole	
Reaction Vessel VI					
115	58.8	0.90	100	132.5	14.2
109	80.1	2.03	102	144.9	22.0
111	101.8	5.70	104	154.6	32
95	118.0	8.86	118	154·6	37
			121	154·6	44
	E = 10.5 kcal./mole				

150° C. the decomposition became too rapid to be followed accurately; yet there was definite indication that the activity of the vessel increased with time (compare Runs 104, 118, and 121).

The effect of poisons on the catalytic surface was also tested in flask V at 60° C. Some gaseous hydrogen cyanide was introduced at a pressure of 2 mm. and pumped off quickly after a short while. Contrary to what is frequently observed with heterogeneous reactions, no poisoning effect of the catalyst could be detected. This is perhaps not surprising in view of the fact that the heterogeneous decomposition of hydrogen peroxide vapour shows no marked specificity as far as the nature of the catalyst is concerned. Treatment of the glass containers with hydrochloric acid has been advocated to help reduce the decomposition of hydrogen peroxide solutions. This was also tried under the same conditions by admitting gaseous hydrogen chloride into the reaction vessel. After quick evacuation the first hydrogen peroxide vapour introduced decomposed instantaneously, presumably owing to oxidation of the hydrogen chloride. Then, after thoroughly outgassing the system, the reaction slowed down considerably: $t_{½} = 180$ min. as compared with 8 min. originally. No further tests were made to find out how long this effect lasted.

III. Decomposition on Quartz

The thermal decomposition of hydrogen peroxide vapour on a quartz surface was investigated for the first time by Elder and Rideal (5). They reported a zero-order reaction at 85° C. but the unusual feature was that the decomposition stopped abruptly at about 15% completion; this was interpreted as due to inhibition by oxygen. Later Kistiakowsky and Rosenberg (11) tried to repeat these experiments. They were unable to get reproducible results although they observed no stopping of the reaction short of complete decomposition. Recently Mackenzie and Ritchie (13) have published extensive results on the same subject in the temperature range 15° to 140° C. Again in all cases the decomposition was complete. The present investigation suggests the following explanation for the phenomenon observed by Elder and Rideal. In their apparatus the quartz vessel at 85° to 95° C. was connected, through a fine capillary tubing, to a soft-glass system kept at 120° C. They assumed a very rapid decomposition of the vapour contained in the connecting tubes; yet this may have been what they were actually measuring. To obtain the 'infinity' reading they had to heat the reaction vessel to a much higher temperature, presumably because the decomposition on the quartz was unmeasurably slow or was preceded by an induction period. This would also explain why on freezing out the hydrogen peroxide left in the system and pumping off the oxygen another 15% decomposed. Mackenzie and Ritchie worked at pressures less than 1 mm. with two different cylindrical quartz vessels having volumes of 21.75 and 31.37 ml. and active surfaces of 42 and 54 sq. cm. respectively. In general the reaction was bimolecular with respect to the peroxide pressure. The conditions for the present work were somewhat different.

Reaction Vessel VII and VIII

The first flask used was made of transparent silica (Vitreosil) connected to a graded seal. The results given in Table V show that the reaction was of the first order with about the same rates as on Pyrex. An outstanding feature, however, was the existence of a sort of induction period, during which the decomposition was very slow (Fig. 5). The length of this induction period decreased with increasing temperature until it had practically disappeared at about 175° C. However, no exact limit can be assigned there because of the time required for filling the vessel and for allowing the vapour to reach thermal equilibrium. To find out whether or not this peculiarity was specific of quartz, a second flask of the same dimensions but of different make (Amersil) was used. The reaction rates were different but the induction period persisted.

TABLE V

REACTIONS IN QUARTZ VESSELS

Run No.	T, °C.	$k \times 10^3$/sec.*	Induction period, sec.
Reaction Vessel VII (Vitreosil)			
160	105	0.42	750
169	125	1.05	430
158	150	3.2	100
166	175	5.6	20
156	205	12.1	0
163	215	17.2	0
162	220	19.6	
	$E = 12.2$ kcal./mole		
After fusing			
198	150	1.14	0
194	185	3.9	0
195	250	15.6	0
196	275	33.8	0
	$E = 11.6$ kcal./mole		
Reaction Vessel VIII (Amersil)			
191	81	3.2	360
193	100	6.7	120
192	152	37.5	0
	$E = 10.3$ kcal./mole		

* *The rate constants were calculated from the first-order portion of the curves only.*

Finally the first flask was fused thoroughly in the blast of an oxygen torch until the quartz became incandescent. This treatment slowed the rate of decomposition to about one-half of its original value and at the same time caused the phenomenon of induction to disappear. The temperature factor of the reaction on quartz in both flasks gave an apparent activation energy of about 12 kcal. per mole.

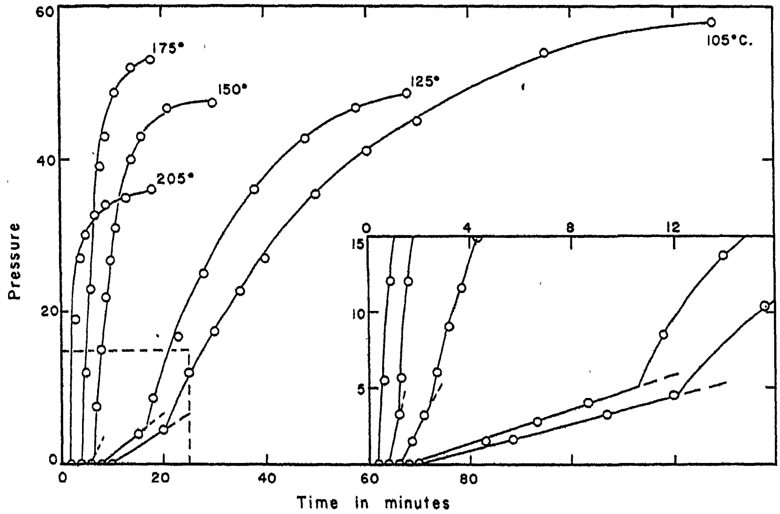

FIG. 5. *Decomposition curves for reaction vessel VII with enlarged section showing the induction periods.*

IV. DECOMPOSITION ON METALS

Most metals, especially when finely divided, are very good catalysts for the decomposition of liquid hydrogen peroxide. There are however a few excepions such as aluminum, which is relatively inactive so that containers made of it are currently used for storing concentrated solutions of hydrogen peroxide. Pure block tin is also claimed to be quite inert in this respect. It was thought worth while to investigate the effect of these metals on the vapour.

Reaction Vessels IX and X

Because of the difficulty involved in making metal containers of the suitable size and shape, and capable of standing reduced pressure, ordinary one-litre Pyrex flasks were covered inside with pure tin and pure aluminum mirrors deposited by the evaporation method. The coatings were made as thick as feasible by this technique; still, from the point of view of catalysis, such a surface may be quite different from that of a solid metal. The decomposition was followed at only three temperatures in each case but the rates could always be duplicated fairly accurately. As shown by the results (Table VI), the activity of both metals is comparable with that of soft glass and quartz. There is however some uncertainty regarding the values of the activation energy.

TABLE VI

DECOMPOSITION ON METALLIZED SURFACES

Reaction vessel IX (Tin)			Reaction vessel X (Aluminum)		
Run No.	T, °C.	$k \times 10^3$/sec.	Run No.	T, °C.	$k \times 10^3$/sec.
289	72.2	1.12	294	96.5	1.60
287	97.6	3.3	296	129.4	7.7
288	117.3	10.7	298	153.0	12.6
E = 13 kcal./mole			E = 12 kcal./mole		

Discussion

It is obviously impossible at present to account for all the above results. Certainly it would be unwise, in an investigation of this kind, to draw general conclusions from a few particular observations since they may well be fortuitous. For instance, zero-order reactions seem to arise whenever there is a very rapid decomposition on some active centre. Only when data on the diffusion of hydrogen peroxide vapour become available will it be possible to account quantitatively for these phenomena. One particular Pyrex vessel gave reactions with a negative temperature coefficient, possibly owing to a progressive alteration of the surface. In spite of the usual treatments the results remained erratic. Previous workers in this field have encountered a similar situation. Like other fundamental reactions apparently simple, the decomposition of hydrogen peroxide is complex in nature. From the predominance of surface effects and the constant temperature coefficient it would appear that the homogeneous decomposition of the peroxide vapour is still unmeasurably slow at 700° K; this points to a rather large energy of activation. Whatever the mechanism of the reaction there is little doubt that the initial step is through breaking of the O–O bond. Experimental evidence of this has been reported recently (7) in the decomposition of tertiary alkyl peroxides, where the case is much less clear-cut. Now, a number of conflicting values are given in the literature for the dissociation energy of peroxides (not to be confused with the O–O bond energy (16, p. 53)). By a spectroscopic method Geib (6) found 52 kcal. for the dissociation:

$$H_2O_2 = OH + OH \ .$$

Essentially the same result is obtained from the following thermochemical and spectroscopic data:

$$\begin{array}{lll}
H_2O_2 & = H_2O + 1/2\ O_2 & \Delta H = -24 \text{ kcal. } (14, 15) \\
H_2O & = OH + H & \Delta H = 118.2 \text{ kcal. } (4) \\
H + O & = OH & \Delta H = -100.1 \text{ kcal. } (4) \\
1/2\ O_2 & = O & \Delta H = 59.1 \text{ kcal.} \\
\hline
H_2O_2 & = 2OH & \Delta H = 53.0 \text{ kcal.}
\end{array}$$

Lewis and von Elbe (12, p. 385) reported a substantially lower value, 43 kcal., while Ubbelohde (19) used 48 kcal., but in neither case was it mentioned on what evidence. Values ranging from 51 to 66 kcal. (3, 20) have been found for the dissociation of various organic peroxides although it can be argued that in these compounds the O–O bond is stabilized by transfer of negative charges to the oxygen atoms. Therefore 52 kcal. seems a plausible figure for the dissociation of hydrogen peroxide. Assuming that the homogeneous decomposition proceeds unimolecularly, this would represent a lower limit for the energy of activation. However, it has not yet been possible to determine the nature of the gas reaction because of the overwhelming importance of the catalysis at all temperatures and on any surface. Semenoff (17, p. 419) believed that it would be a chain reaction on account of its resemblance with the photochemical decomposition (1), which has been shown to take place through very long chains (of the order of 10^4 to 10^7 units) in solution at least. Previous investigations (2, 13) have indicated, on the contrary, that long chains play no great role in the case of the vapour. Still it is possible that the conditions were not favourable then to the formation or the propagation of chains.

The catalytic decomposition of hydrogen peroxide is peculiar in that there is no very specific action of the active surface. To be sure, the observed rates vary appreciably from one catalyst to another as shown above but, on the whole, results of the same order of magnitude were found with such widely different surfaces as glass, metals, and paraffin oil. It seems like a case of physical rather than chemical adsorption. The polar character of the hydroxyl group leads to adsorption on any surface. The hydrogen peroxide molecule is thus oriented and the relatively weak O–O bond is strained so that only a low thermal activation is required for the dissociation. All surfaces will therefore decompose the peroxide vapour at an appreciable rate at moderate temperatures. Even so, the values observed for the apparent energy of activation, 8 kcal. and even as low as 4 in some instances (13), seem very small indeed in view of what has been said above. This is a fairly sure indication that the mechanism of the normal reaction is modified by the catalyst. Experimental data are lacking on the adsorption of hydrogen peroxide vapour, but off-hand one would expect its temperature coefficient to be about the same as for water, on the basis of the polarity of the two molecules.

Inspection of the curves in Figs. 6 and 7 reveals the absence of correlation between the apparent energy of activation and the reaction velocity. For quartz, soft glass, and the two metals investigated, the slopes are generally the same as for untreated Pyrex, whereas the rate constant changes by a factor of 15 between the two extreme cases. Very likely this is caused by variation in the number of adsorbed molecules, related to factor A in the modified Arrhenius equation:

$$k = A\, e^{-(E-\lambda)/RT} ,$$

where E is the true energy of activation and λ, the energy of adsorption of the reactant. The slowing-down effect caused by fusing is no doubt due to a smoothing of the surface. As already mentioned, freshly fused glass shows a marked tendency to become more active on ageing until it reaches a sort of equilibrium state. This behaviour is possibly the result of incipient crystallization in a supercooled medium. On the other hand, the activation caused by acid washing has generally been attributed to a selective solution of the more soluble components of the glass, which leaves a sponge-like structure. This view is substantiated by the observation that a simple washing of the fused surface with hot water (Vessel III) increased its activity considerably. The present investigation was completed when the attention of the author was drawn to the fact that the common practice of cleaning glassware with chromic acid has been shown to leave a film of chromium oxides which are not removed even by numerous washings (Prof. F. G. Keyes, M.I.T.; private communication). Consequently the reaction rates reported above must be too high. It is not believed, however, that the general trend of the results was appreciably affected. At any rate curves *C* and *G* (Fig. 6) seem to be definitely in a class by themselves.

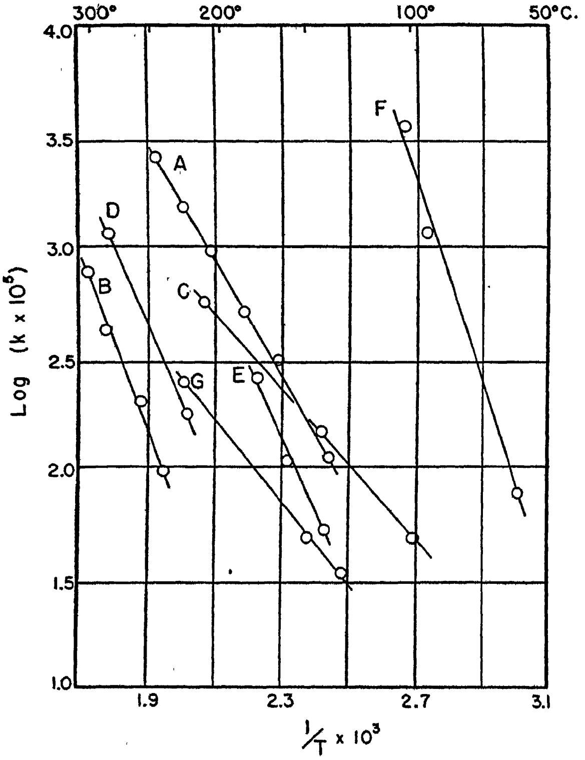

FIG. 6. *Temperature coefficient of the reactions in Pyrex vessel III variously treated. A = normal; B = fused; C = treated for five minutes with hot chromic acid; D = fused again; E = washed with hot water; F = coated with salt; G = etched with hydrofluoric acid.*

The large increase in the amount of hydrogen peroxide present in the reaction system proves beyond doubt that adsorption is responsible for the zero-order reactions on a Pyrex surface (Run 52) as well as for the induction periods on quartz. Complete saturation of all the active centres may have occurred in the former case. Zero-order decompositions were found by Elder and Rideal (5) for the peroxide vapour on glass and by Williams (21) for the liquid on a quartz surface. Short induction periods have also been observed in the thermal decomposition of diethyl peroxide (10). No attempt has been made here to calculate the absolute reaction rates. The mere fact that two similar vessels (V and VI) made from the same batch of glass and treated exactly alike had rates differing by a factor of four, and apparent heats of activation differing by 10%, shows what little significance such calculations would have.

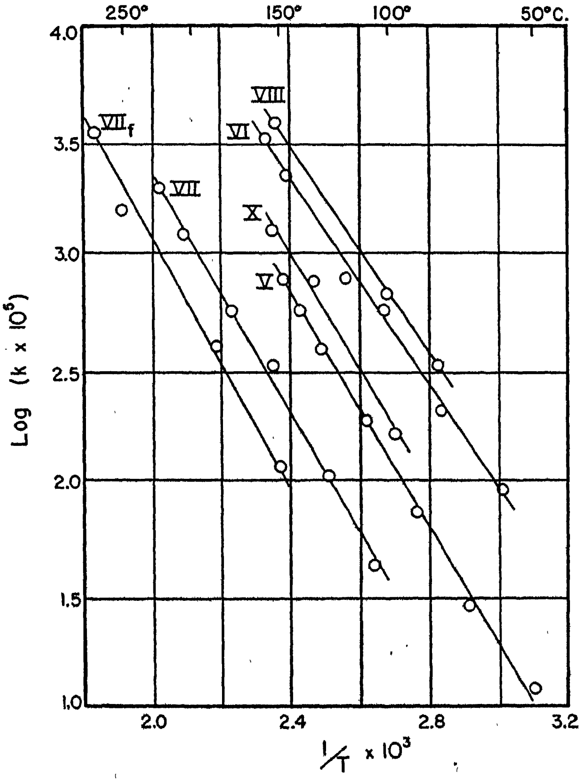

FIG. 7. *Temperature coefficient of the decomposition on soft glass, quartz, and aluminum surfaces. The numerals refer to the reaction vessels.*

Acknowledgment

The author wishes to express his indebtedness to Dr. Cyrias Ouellet for his continued interest in this work and for many helpful discussions.

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STUDIES ON REACTIONS RELATING TO CARBOHYDRATES AND POLYSACCHARIDES

LXII. EFFECT OF HOT ALKALI ON THE NITRATES OF STARCH, AMYLOSE, AND AMYLOPECTIN[1]

By W. R. Ashford[2] and Harold Hibbert[3]

Abstract

The nitrates of starch, amylose, and amylopectin were treated with hot aqueous sodium hydroxide solution and the effect of this treatment upon each noted. This treatment does not cause appreciable denitration, nor does it result in a usefully stable nitrate. The nitrates of the starches are more resistant to alkali than is cellulose nitrate. Amylose nitrate appears to resemble cellulose nitrate in being more alkali-labile than either whole starch nitrate or amylopectin nitrate; this is consistent with its linear chain structure. The greater stability of amylose nitrate as compared to amylopectin nitrate is paralleled by a greater alkali-lability of the former, which indicates that the inherent instability of starch nitrate is not due to the presence of free terminal aldehyde groups present either in native starch or formed during the nitration process.

Introduction

If starch is treated with hot dilute sodium hydroxide solution, there is formation of simple organic acids and reducing substances. Assuming a potential free aldehyde group at the terminus of the starch molecular chain, then these reducing substances could be produced in a manner analogous to their production in the reaction between aqueous alkali and an aldose sugar (2). Taylor *et al.* (6) and Schoch and Jensen (4) have defined this sensitivity of starch to alkali as 'alkali-lability' and according to the latter authors this lability is expressed as 'alkali-number', which represents the number of millilitres of 0.1 N sodium hydroxide consumed by 1 gm. of starch when heated in this solution for one hour at 100° C. Alkali-lability serves only to indicate whether the aldehyde content of the starch has remained constant or whether it has increased or decreased. This in turn serves to indicate hydrolytic changes (3). Starches that have not been subjected to hydrolysis have a negligible or low alkali-lability (6). Schoch believes that the alkali consumption results from the sole interaction of the alkali with free terminal aldehyde groups, and he has shown (5) that the α-1,4- and the β-1,4-glucosidic linkages in maltose and cellobiose respectively are stable to alkali.

During the work described by the authors (1) on the fractionation and nitration of starch it became of interest to observe the effect of hot aqueous

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[2] *Holder of a Fellowship under the National Research Council of Canada, 1942–43. Present address: The Research Laboratories, Dominion Rubber Co. Ltd., Guelph, Ontario.*

[3] *Late Professor of Chemistry, Division of Industrial and Cellulose Chemistry, McGill University.*

sodium hydroxide upon amylose and amylopectin (separated by the adsorption of the amylose upon cotton cellulose) and upon the nitrates of these substances as well as whole starch nitrate. No attempt was made to duplicate Schoch's 'alkali-lability' method, a stronger alkali solution and a shorter time of reaction being employed. However, the same fundamental reaction should take place as that described by the latter author.

By a casual observation of the reaction between alkali and starch nitrate, one would expect two possible reactions, the first, a denitration and the second, subsequent to or coincident with the first, a reaction similar to that which Taylor and Schoch have described for starch. Experiments showed, however, that under the conditions used, namely, treatment of the nitrate for 15 min. with hot sodium hydroxide solution (0 3928 *N*), there is no denitration in the case of starch nitrate, amylose nitrate, or amylopectin nitrate. This is quite possible, if, as has been suggested for starch, the alkali attacks only the terminal aldehyde grouping of the starch nitrate molecular chain, leaving the remainder of the chain unaffected. The starch molecule having undergone considerable hydrolysis during the nitration reaction would normally contain an increased number of these terminal aldehyde groups. In the case of whole starch nitrate (Table I) the nitrogen content was slightly greater after alkali treatment than before, while with amylose and amylopectin nitrates the reverse was true. With whole starch at least, it would appear then that the nitrate groups on the nitrated starch chain are stable to alkali. With whole starch nitrate, 70% of the material was dissolved by treatment with aqueous alkali (0.3928 *N*) for 15 min. at reflux temperature. The undissolved residue was a pure white powder when dried, while the solution containing the dissolved nitrate was deep reddish-brown. The residual undissolved material was tested for its stability by means of the Bergmann–Junk test and a value of 10.53 mgm. of nitrogen evolved per gram of nitrate was obtained, indicating very poor explosive properties.

The amylose and amylopectin used in these experiments were obtained by the method previously described (1) whereby the amylose is separated from the amylopectin by adsorbing the former on cotton cellulose, from which it is easily removed by means of boiling water. As shown in Table I, a 250 mgm. sample of amylose was completely solubilized by sodium hydroxide (0.3928 *N*) in 15 min. In the case of amylopectin, complete dissolution did not take place and in neither case was there any appreciable consumption of alkali. When the nitrates of these two substances were treated with alkali there was considerable consumption of alkali, the amylose nitrate using 3.65 milliequivalents and the amylopectin nitrate 2.79 milliequivalents. This would indicate considerable hydrolysis during the nitration. Presumably this involved liberation of additional terminal free aldehyde groups (4, 6) to an equal extent in both cases since the basic chain structure of amylose and amylopectin is considered to be the same (α-1,4-glucosidic linkages). Therefore the nitration of amylose resulted in the formation of more terminal aldehyde groupings than in the case of the nitration of amylopectin.

TABLE I

EFFECT OF HOT ALKALI UPON THE NITRATES OF STARCH, AMYLOSE, AND AMYLOPECTIN

Substance treated	Treatment	Result	Recovered Product
Starch nitrate % N, 12.83	Refluxed for 30 min. with NaOH (0.3928 *N*)	70% nitrate dissolved	% N, 13.32 Abel heat test—25 min. *Bergmann–Junk test—10.53 mgm. N_2 Ash, 0.31%
Starch nitrate % N, 12.83	Refluxed for 30 min. with NaOH (0.1227 *N*)	20% nitrate dissolved	*Bergmann–Junk test—8.12 mgm. N_2
Cellulose nitrate % N, 12.5	Refluxed for 30 min. with NaOH (0.3928 *N*)	Complete digestion to dark red solution	
Amylose	250 mgm. sample refluxed in 25 cc. NaOH (0.3928 *N*) for 15 min.	Complete dissolution. Alkali consumed—negligible	
Amylopectin	As for amylose	Flocculent globules remained undissolved. Alkali consumed—negligible	
Amylose nitrate % N, 13.15	0.5 gm. refluxed in 25 cc. alkali (0.3928 *N*) for 15 min.	Incomplete solution. Alkali consumed—3.65 milliequivalents	% N, 12.95
Amylopectin nitrate % N, 13.25	As for amylose nitrate	Incomplete solution. Alkali consumed—2.77 milliequivalents	% N, 13.02

* *Mgm. of N_2 evolved per 1.0 gm. sample of nitrate.*

In a previous paper (1) it was shown that amylose nitrate is more stable than amylopectin nitrate by means of the Bergmann–Junk test. From the results of the alkali treatment of these two substances it would seem that the higher alkali consumption of amylose nitrate is associated with a greater stability of this substance as compared with a lower alkali-lability of the less stable, amylopectin nitrate. The instability of these polysaccharide nitrates cannot, then, be associated with the presence of free aldehyde groups, a conclusion borne out by the fact that the more stable cellulose nitrate is as readily attacked by alkali as is amylose nitrate and considerably more readily attacked by this reagent than is amylopectin nitrate. The agreement in the ease with which amylose nitrate and cellulose nitrate are attacked by alkali points to a similarity in their structure.

Experimental

A suspension of the nitrate (0.5 gm.) in standard sodium hydroxide solution (25 cc.) was refluxed for 15 min. with intermittent shaking of the flask. Cold distilled water (50 cc.) was then added through the condenser and the solution titrated at 15° C. with standard nitric acid using phenolphthalein as indicator.

In cases where larger amounts of nitrate were used, the undigested portion, after the alkali treatment, was removed by filtration. The alkali was then removed from this material by boiling under reflux with distilled water, for periods of 50 hr.

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STUDIES ON REACTIONS RELATING TO CARBOHYDRATES AND POLYSACCHARIDES

LXIII. THE STABILITY OF MALTOSE AND CELLOBIOSE OCTANITRATES[1]

By W. R. Ashford,[2] T. H. Evans,[3] and Harold Hibbert[4]

Abstract

Cellobiose and maltose were nitrated and their properties studied to note the effect of the difference in glycosidic linkage (β- and α-respectively). Cellobiose octanitrate is more stable than maltose octanitrate as measured by the Abel test, and both are less stable than cellulose and starch nitrates. Neither of the octanitrates is sufficiently stable to permit of the application of the Bergmann–Junk test. If the stability of the cellulose nitrate building unit, namely, cellobiose octanitrate, carries over into its polymeric form, it would be expected that cellulose nitrate (characterized by 1,4-β-glucosidic linkages) should be inherently more stable than starch nitrate (α-1,4-glucosidic linkages).

Discussion

The nitrates of maltose and cellobiose were prepared and studied for the purpose of comparing the properties, particularly stabilities, of the fundamental building units of starch and cellulose respectively. Cellobiose octanitrate has not been characterized previously.

The two major chemical differences between starch and cellulose are (*a*) the type of glycosidic linkage (α- and β- respectively) and (*b*) the presence of branched chains in the former (5, pp. 143-182). It seemed that any difference due to glycosidic linkages (α- or β-) might be made apparent from a study of these disaccharides, and that these would provide a possible explanation of the relative instability of starch nitrate.

The nitrates of maltose and cellobiose were prepared as white amorphous solids in high yields by the nitration method described previously (1). Like the corresponding polysaccharides they were insoluble in water and were precipitated from their solution in concentrated nitric acid by the addition of concentrated sulphuric acid.

The fact that cellobiose nitrate was obtained in higher yields (191%) than maltose octanitrate (183%) indicated that during nitration hydrolysis took place to a somewhat greater extent in the case of the latter, a result to be expected in view of the presence of the α-linkage in maltose (4).

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Contribution from the Division of Industrial and Cellulose Chemistry, McGill University, Montreal, Que. Taken from a thesis submitted to the Faculty of Graduate Studies and Research by W. R. Ashford in May 1943 in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] *Holder of a Fellowship under the National Research Council of Canada, 1942–43. Present address: The Research Laboratories, Dominion Rubber Co. Ltd., Guelph, Ontario.*

[3] *Sessional Lecturer, 1941–43, Division of Industrial and Cellulose Chemistry, McGill University. Present address: The Research Laboratories, Dominion Rubber Co. Ltd., Guelph, Ontario.*

[4] *Late Professor, Division of Industrial and Cellulose Chemistry, McGill University.*

The products were purified by an initial treatment with charcoal and anhydrous sodium sulphate in methanol solution. The maltose derivative was then recrystallized from diethyl ether and the cellobiose derivative from ethanol. The crude nitrates were much more soluble in methanol, ethanol, diethyl ether, etc., than when more highly purified, this being especially true of cellobiose octanitrate. Both substances showed a marked tendency to separate from solution in the amorphous state, but crystallization could be induced by very slow concentration of these solutions at room temperature. The crystalline structure of both compounds appeared to be the same, namely, needles arranged in the form of tiny rosettes.

The melting point of the crude products was very indefinite (70° to 90° C.) owing to the presence of glucose pentanitrate (m.p. 10° C.). The purified maltose octanitrate melted at 163° to 164° C. and the cellobiose octanitrate at 154° to 155° C.

Properties of the Nitrates

Their analyses (Table I) corresponded to those of the pure octanitrates.

TABLE I

PROPERTIES OF MALTOSE AND CELLOBIOSE OCTANITRATES

Property	Maltose octanitrate	Cellobiose octanitrate
Nitrogen content, %	15.87 (theoretical—15.95)	15.91
Molecular wt (Rast method)	699 (Calculated—702)	698
Abel test, min.	18	32
Bergmann–Junk	Both products too unstable to stand the test	
Alkali-lability*	7.97	13.82

* *Milliequivalents of sodium hydroxide (0.0567 N) consumed during 30 min refluxing.*

The Abel test indicated that the cellobiose nitrate was the more stable, while neither compound was of sufficient stability to withstand the Bergmann–Junk test for the usual period (two hours).

On alkali treatment (2), cellobiose octanitrate consumed more alkali than did the maltose compound, 13.82 and 7.97 milliequivalents of sodium hydroxide (0.0567 *N*) respectively. This result is to be compared with those of previous experiments (2) where cellulose nitrate consumed more alkali than starch nitrate.

On the basis of these results it was concluded that cellobiose octanitrate possesses slightly greater stability than maltose octanitrate and that, if this difference is cumulative, then cellulose nitrate should be inherently more stable than starch nitrate.

Experimental

Preparation of Cellobiose

The cellobiose was prepared from cellobiose octaäcetate by hydrolysis with sodium methylate in absolute methanol (3).

Nitration

Cellobiose (13 gm.) was nitrated, according to the procedure used for whole starch (1, 6), with nitric acid (95 cc., sp. gr. 1.5) and sulphuric acid (110 cc., 96.5%). The cellobiose dissolved immediately in the nitric acid and the nitration was allowed to proceed for one hour. Concentrated sulphuric acid precipitated the nitrate as a gummy mass, which was ground in a mortar with ice-water to yield a pulverulent mass. The product was filtered and washed until acid-free by refluxing in distilled water for at least 25 hr.

Maltose (Kahlbaum) was nitrated in a manner identical with that used for cellobiose.

Both nitrates were white amorphous solids, insoluble in water. The crude products were unstable, especially the maltose preparation, which decomposed slowly at 50° to 55° C.

The yields of crude products were: maltose nitrate, 183.2; cellobiose nitrate, 191.0% (theoretical, 205.3%).

Purification

(*a*) *Maltose octanitrate.*—A methanolic solution of crude maltose octanitrate was treated with charcoal at 40° to 50° C., then dried with anhydrous sodium sulphate. The removal of methanol under reduced pressure at room temperature caused the nitrate to separate in crystalline form (needles in rosette formation) (m.p. 95° C.). The crude crystals were dissolved in diethyl ether, from which glucose pentanitrate and maltose octanitrate were separated by fractional crystallization. The ether solution of the crude crystalline product was allowed to stand at room temperature, and, on evaporation of the solvent, deposited a good yield of crystalline maltose octanitrate, leaving the glucose pentanitrate in solution. Recrystallization from ether did not change the melting point (163° to 164° C.) Reported value, 163° to 164° C. (6).

(*b*) *Cellobiose octanitrate.*—The crude product was treated with methanol, charcoal, and anhydrous sodium sulphate as was the maltose octanitrate. The first crop of crude crystals had an indefinite melting point of 85° to 95° C. These crystals were recrystallized from ethanol and gave a product melting at 149° to 150° C. Recrystallization from ether–methanol solution (2 : 1) raised the melting point to 154° - 155° C., which did not change on subsequent recrystallizations.

Properties of the Nitrates

The nitrates were examined for their nitrogen contents, molecular weight, stability, and their alkali-lability, with the results shown in Table I. Methods for nitrogen content and stability were those described previously (1). Molecular weights were determined by the method of Rast.

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TERTIARY MERCAPTANS AS MODIFIERS IN GR-S POLYMERIZATIONS[1]

BY MAURICE MORTON[2] AND R. V. V. NICHOLLS[3]

Abstract

Tertiary octyl, decyl, dodecyl, and hexadecyl mercaptans were investigated as modifiers in GR-S polymerizations.

The rate of disappearance of these modifiers followed a first-order rate equation during the first half of the polymerization, in accordance with the theory of chain-transfer reactions. During the latter part of the reaction, an increased rate of disappearance generally occurred. A mechanism is suggested.

The rate of disappearance increased with decreasing chain-length of the mercaptan. The intrinsic viscosities and molecular weight distributions of the polymers obtained at different conversions were related to the activity of each mercaptan as a modifier. Values for the regulating index of each mercaptan were calculated.

The slow rate of disappearance of tertiary hexadecyl mercaptan leads to the formation of polymer that is relatively homogeneous in molecular weight, and this mercaptan is therefore a desirable modifier. However, after 50% polymerization, the regulator action shows a marked acceleration, leading to the formation of progressively lower molecular weight polymer and resulting in a spread in the molecular weight distribution.

Introduction

The regulation of molecular size during polymerization by compounds, such as mercaptans, is usually termed 'modifier action'. The mechanism of such modifier action has been the subject of intensive study, especially in connection with the GR-S polymerization. A great deal of evidence has been presented in support of the view that modifiers, such as the mercaptans, act as chain-transfer agents (11, 13). This mechanism presupposes that the growing polymer chain is terminated by a hydrogen atom from a mercaptan molecule, the remaining mercaptan free radical acting as an initiator of a new polymer chain.

On the basis of such a chain-transfer mechanism, Ewart, Smith, and Hulse (4) developed a kinetic relation for the rate of disappearance of mercaptan during polymerization. From this kinetic relation they also derived the manner in which the molecular weight of the polymer formed should vary during the course of the polymerization. Their experimental data on the emulsion polymerization of butadiene showed good agreement with theory at low conversions.

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[2] *Graduate student in chemistry, and holder of a Studentship and a Fellowship from the National Research Council of Canada. At present, Honorary Lecturer, Department of Chemistry, McGill University.*

[3] *Associate Professor of Chemistry.*

By means of a simple mathematical treatment of the polymerization reaction, Ewart *et al.* derived a function that they termed the 'regulating index' of a modifier. This function is defined as follows:

$$r = -\frac{d \ln R}{dP}, \qquad (1)$$

where P = number of grams of polymer formed per gram of initial monomer, at any time.
R = concentration of regulator, expressed as moles of regulator per gram of initial monomer,
r = a constant known as the 'regulating index',

The value of r thus represents the activity of any modifier in its action as a chain-transfer agent. From this a relation was derived between the regulating index of a modifier, its concentration at any time, and the polymer chain-length being formed at that time, thus:

$$M_R = \frac{1}{rR}, \qquad (2)$$

where M_R = number-average molecular weight of polymer produced at that particular instant.

Ewart *et al.* termed M_R the 'regulator theory molecular weight', but it is evident that it is in fact identical with the number-average molecular weight, in the absence of chain branching.

It is important to note that the derivation of this regulating index of modifiers is based upon one basic assumption made by Ewart *et al.*, and expressed thus:

$$-\frac{dR}{dP} = rR . \qquad (3)$$

Such an assumption could be valid under conditions where the rate of polymerization is independent of monomer concentration. This condition is actually found to be true, at least up to conversions of 70%, in the case of the GR-S emulsion polymerization, although it is contrary to the classical rate equation derived for bulk polymerization systems. The classical expression for the propagation step in polymerization is represented by

$$\frac{dP}{dt} = k_1 [A^\cdot] [M] ,$$

where $[A^\cdot]$ = concentration of active centres,
$[M]$ = concentration of monomer.

For the GR-S system, assuming monomer concentration remains constant, this becomes

$$\frac{dP}{dt} = k_2 [A^\cdot] . \qquad (4)$$

The rate equation for modifier consumption, based on a chain-transter mechanism, is represented by

$$-\frac{dR}{dt} = k_3 [A^\cdot] R . \qquad (5)$$

It can be seen that by dividing Equation (5) by Equation (4) there is obtained an expression identical with Equation (3).

It must be emphasized that the above deductions are applicable only to a case such as the GR-S polymerization, where the emulsion system apparently prevents the depletion of monomer from affecting the rate of polymerization until high conversions are reached.

Tertiary aliphatic mercaptans have been known for some time to possess the ability of regulating the molecular size of polymers and of acting as promoters in GR-S polymerization. The term 'promoter' refers to the well known fact that mercaptans have the ability of enhancing the effect of a catalyst such as potassium persulphate, and thus increasing markedly the rate of polymerization. Hence it was considered of interest to investigate more fully the action of various tertiary mercaptans as modifiers, in an attempt to establish a regulating index for each and to correlate molecular size of the polymer with each regulating index. The data presented in this paper have been obtained for the purpose of determining as carefully as possible exactly how the character of the polymer changes in the course of polymerizations carried out with various tertiary mercaptans. The studies to date have been carried out only on Sharples' tertiary octyl, decyl, dodecyl, and hexadecyl mercaptans.

Experimental Procedures

The following methods of investigation were used in the evaluation of this series of tertiary mercaptans:

1. GR-S polymerization using various tertiary mercaptans at several different initial concentrations;
2. Determination of rate of polymerization;
3. Determination of rate of mercaptan disappearance;
4. Characterization of the polymer,
   (*a*) Coagulation and drying of the polymer,
   (*b*) Sol–gel separation,
   (*c*) Determination of the intrinsic viscosity of the polymers obtained at different conversions,
   (*d*) Determination of a precipitation-distribution function for the polymers obtained at different conversions.

The experimental technique and materials used are described below.

1. Polymerization

Apparatus

The polymerizations were carried out in the standard 4-oz. round-form bottles, with metal screw caps. The caps were fitted with Neoprene liners, which were always extracted with hot acetone before use. The bottles were rotated end over end in a water-bath maintained at 50° ± 1° C., and fitted with a horizontal shaft to which were attached the bottle clamps at a radius of about 8 in. The speed of rotation was about 30 r.p.m.

It might be stated at this point that several attempts were made, at the beginning of this investigation, to use the tube polymerization method as outlined by Fryling (6). It was found, however, that erratic results were obtained with this technique, some kind of inhibiting action being noticeable and leading to low, non-reproducible conversion rates. Strangely enough, although this erratic effect occurred with the use of tertiary mercaptans, it was not noticeable when OEI (technical *n*-dodecyl mercaptan) was used as a modifier. No explanation has been offered for this behaviour.

Materials

The Mutual Recipe was used, with variations only in the kind and amount of mercaptan used, as follows:

POLYMERIZATION RECIPE (PARTS BY WEIGHT)

Water	180
Soap	6
Potassium persulphate	0.3
Mercaptan	Variable
Styrene	25
Butadiene	75

The soap used was the household variety of Ivory Flakes, stored in the dark in a tightly stoppered container in order to avoid peroxide formation. Periodic control runs were carried out to check the uniformity of the soap flakes.

Potassium persulphate used was Merck's Analytical Reagent grade.

Styrene* used was received from the Dow Chemical Company of Canada, Sarnia, Ont. This styrene was inhibited with 10 p.p.m. of *p*-tertiary butyl catechol. After several control runs it was found that identical results were obtained whether the styrene was redistilled, or used as received. Hence, in all runs, the styrene was used as received; i.e., with the inhibitor present.

The butadiene* used was received from the Canadian Synthetic Rubber Limited, Sarnia, Ont. It was purified by bubbling through a 2 *N* solution of sodium hydroxide to remove any inhibitor (300 p.p.m. of *p*-tertiary butyl catechol), and then through a glass U-tube, packed with glass wool and kept at −5° C. The purified butadiene was collected in a dry ice – acetone trap, from which it was apportioned to the required charges.

The tertiary mercaptans* were obtained from the Sharples Chemicals Inc., Philadelphia, Pa. The following mercaptans were used:

Tertiary octyl mercaptan	(Sharples 2-B)
Tertiary decyl mercaptan	
Tertiary dodecyl mercaptan	(Sharples 3-B)
Tertiary hexadecyl mercaptan	(Sharples 4-B)

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* *We desire to acknowledge donations of generous samples of these materials.*

The amounts of these mercaptans obtainable at the time were too small for a purification by fractionation, except in the case of the 3-B mercaptan, of which a plentiful supply was available. Hence the 3-B mercaptan was fractionally distilled under reduced pressure, and the main fraction, which had a constant refractive index, was collected for use. The physical constants of the main fraction obtained from the 3-B mercaptan are shown below, together with the mercaptan content, as determined by amperometric titration with silver nitrate, according to the method of Kolthoff (8).

This main fraction constituted over 90% of the mercaptan as received.

Physical constants of main fraction from Sharples 3-B mercaptan: specific gravity (d_4^{20}), 0.867; boiling point (16 mm.), 112° C.; refractive index (N_{25}^{D}), 1.4655; mercaptan content (as $C_{12}H_{25}SH$), 98.1%.

The mercaptan content of the other three mercaptans was also determined, and was found to be as follows: octyl, 95.6; decyl, 97.0; hexadecyl, 97.6%.

Procedure

A total charge of 98.0 gm. was used for all bottles, leaving a free space of 10 to 15 cc. The aqueous solution containing the soap and potassium persulphate was added first, then the styrene, containing the required mercaptan. The bottle was then chilled in ice-water, and a slight excess of liquid butadiene added. The cap was then loosely placed on the bottle, and the excess butadiene allowed to evaporate until the bottle assumed the desired weight. It was then capped tightly, a rubber glove being used to apply the required torsion on the screw cap to prevent leakage. All bottles were tested to 200 lb. per sq. in. pressure before use. Any leakage could usually be detected when the bottles were first placed in the water-bath, but, in addition, each bottle was reweighed at the conclusion of the run.

2. Determination of Rate of Polymerization

Procedure

At periodic intervals (usually after 2, 4, 6, 9, and 12 hr.) duplicate bottles were removed from the water-bath and chilled in ice-water at 0° C. Each bottle was then opened and 0.1% hydroquinone added, based on initial monomer weight, as an inhibitor of any further polymerization. The latex was then sampled by the 'stopcock method' as described by Medalia (10), care being taken to shake the latex vigorously before sampling. The size of the sample was usually about 10 gm., which could be weighed on a torsion balance with an accuracy of ± 0.02 gm. It was found necessary to use a 'venting factor' owing to loss of butadiene during sampling, especially for low-conversion polymers. This factor was determined as follows.

The loss in weight of the bottle containing the latex was taken as the true weight of the latex removed. The sample of latex, which was usually in a small beaker, was then warmed gently (30° to 40° C.) and shaken until it showed no further loss in weight. The final weight of this latex sample was then considered as the 'vented weight'. All subsequent work on the vented latex was always corrected by the use of the proper factor in order to calculate all results on the basis of the original latex in the bottle. The sample of latex thus obtained was used both for the determination of the per cent conversion and for the analysis of the amount of remaining mercaptan.

The conversion was determined by the total solids method. A 1 gm. sample of the vented latex was dried to constant weight at 105° C. in one or two hours. Duplicate determinations were usually carried out on the contents of each bottle. Agreement between duplicate determinations was of the order of ± 2 parts per thousand for high conversion latex and somewhat worse for low conversion latex, apparently owing to difficulty in uniform sampling due to the instability of the emulsion at low conversions. Agreement between duplicate bottles was of the order of ± 5 parts per thousand or better for high-conversion latex and somewhat worse for low conversion latex.

3. Determination of Residual Mercaptan

A portion of the same sample obtained for the determination of the conversion was used for mercaptan analysis. The method used was the amperometric titration with silver nitrate, using a rotating platinum electrode, as described by Kolthoff and Harris (8). The latex was coagulated by dropwise addition to 100 ml. of rapidly stirred absolute ethanol. In order to complete the coagulation and to reduce the residual persulphate, there was added 1 ml. of a solution that was 1 N with respect to sulphuric acid and 0.1 N in ferrous ammonium sulphate. Size of the latex sample was usually 5 gm., and the strength of the silver nitrate solution was either 0.005 N or 0.002 N, depending on the amount of mercaptan to be determined. Since the titrations were carried out in the presence of coagulated polymer, care was taken to have a fine, curdy precipitate, with no lumps that might trap some of the mercaptan. Duplicate determinations on the same sample of latex were found to agree within ± 5 parts per thousand, while duplicate bottles gave results that agreed within ± 10 parts per thousand.

4. Characterization of Polymer

(a) *Coagulation and Drying*

Before proceeding with the characterization of the polymer, it was necessary to coagulate the latex and to thoroughly dry the resulting polymer. The coagulation was carried out by pouring the latex slowly into rapidly agitated *n*-butanol, and the resulting curd was washed well with distilled water to remove all traces of soap. The wet polymer was then dried *in vacuo* at 40° C. It was found that, at 5 mm. pressure, between 48 and 72 hr. of drying was sufficient for polymer samples under 10 gm. in weight. Owing to the coagulation in alcohol, it was not possible to incorporate any antioxidant into the polymer, since the antioxidant would dissolve readily in the alcohol. Hence the polymer obtained was never allowed to stand longer than two weeks, even in the dark, as it was feared that some deterioration might result. It was actually found that polymer that had originally been completely soluble in benzene developed a considerable proportion of insoluble gel on standing for two months at room temperature in the dark.

(*b*) *Sol – Gel Separation*

Solutions of the polymers were usually made up by placing finely shredded polymer in reagent grade benzene and allowing to stand for at last 48 hr. in the dark. In the case of polymer of low molecular weight ('sticky polymer'), the solution was made up with 2.1 gm. of polymer in 350 cc. of benzene. For polymer of higher molecular weight, the solution consisted of 1.4 gm. polymer in 350 cc. of benzene. This procedure usually yielded solutions having the proper concentration both for intrinsic viscosity determinations and for precipitation studies. The solutions, contained in stoppered flasks, were gently swirled on the second day, in order to promote mixing. After 48 hr., the solutions were examined for any visible gel, and then very carefully decanted through a layer of glass wool supported on a 100 mesh stainless steel wire screen. The amount of insoluble material was then determined indirectly from the concentration of the filtered solution. This was done by evaporating 25 cc. of this solution to dryness in an oven at 70° C.

The above method usually gave a good separation of sol from gel, since it was found that the resulting solution could pass easily through a coarse Pyrex frit. This test, according to Baker and Mullen (2) is very sensitive to dispersed gel, since as little as 0.5 mgm. of highly swollen gel will clog the frit completely. In one or two cases it was found that the gel was apparently so fragile that some of it passed through the glass wool and into the solution, preventing the latter from being passed through the Pyrex frit. In these cases it was sometimes found desirable to carry out a sol–gel separation in a Baker Cell (2) where the gel received more gentle treatment. Obviously, in this type of investigation, the accurate determination of gel content is not of great consequence, since the real interest lies in polymers that are completely soluble and capable of characterization as to molecular size.

(*c*) *Determination of Intrinsic Viscosity*

The viscosities of the polymer solutions were determined by means of an Ostwald type viscometer. The viscometer used had an outflow time of about 130 sec. for pure benzene, so that the kinetic energy correction was very small. This correction was determined by calibrating the viscometer by means of three different liquids, viz., benzene, *n*-heptane, and carbon tetrachloride, and applying the standard viscosity equation (1, 3), which has the form

$$\gamma = Ct - \frac{B}{t},$$

where γ is the kinematic absolute viscosity,
C is the instrument constant,
B is the kinetic energy constant,
t is the outflow time.

Hence by using any two liquids whose kinematic viscosity is accurately known, the two constants may be evaluated.

The temperature used was 25° C., which was maintained in a water-bath kept within ± 0.01° C. The concentration of the polymer solutions ranged from 0.4 to 0.6 gm. per 100 cc. of benzene, depending on the molecular weight of the polymer. This concentration was determined for each polymer sample by evaporating 20 cc. of the solution to dryness at 70° C. In order to enable the extrapolation of the specific viscosity to zero concentration, as required for the evaluation of the intrinsic viscosity, it was necessary to determine the viscosity of each polymer sample at three different concentrations. Thus, in addition to the polymer solution prepared originally, two others were obtained from it by aliquot dilution with benzene, using dilution ratios of 1 : 1 and 1 : 3, respectively.

(*d*) *Determination of a Precipitation Distribution Function for Polymers Obtained at Different Conversions*

Since the value of a viscosity average molecular weight is so greatly dependent on the type of molecular weight distribution, it was felt that a measure of the heterogeneity of each polymer sample would be of assistance in evaluating changes in viscosity. A simple method of fractional precipitation was used for this purpose, as outlined by Wall (12). Twelve fractions of 15 cc. each of polymer solution were used to which were added 10 cc. of a mixture of various proportions of methanol and benzene. The proportions of methanol and benzene in the precipitating solutions were such that the final volume per cent of methanol in the final solution ranged from 16.7 to 33.3%. The fraction of polymer remaining in solution, denoted by f was then plotted against the volume per cent of methanol in solution, denoted by Φ, and a solubility curve thus obtained. By differentiating this solubility function, and plotting the negative slope, $-\frac{df}{d\Phi}$, against the volume per cent methanol, Φ, a precipitation distribution curve was obtained. According to Wall (12), such a precipitation distribution curve has been found to agree fairly closely with the actual molecular weight distribution existing in the polymer sample.

Results and Discussion

Rates of Polymerization and of Mercaptan Disappearance

Data on the rates of polymerization and rates of mercaptan disappearance for all the mercaptans used are shown in Tables I to IV, inclusive. It can be seen that the rates of polymerization were approximately the same in the case of the decyl, dodecyl, and hexadecyl mercaptans, amounting to an average of 6% conversion per hour up to 72% conversion. This is in agreement with the rate generally obtained for the usual GR-S polymerization. The octyl mercaptan exhibited a slightly lower rate of polymerization, i.e., about 5% per hour up to 60% conversion. It is interesting to note that, after 12 hr., the rate of polymerization dropped considerably, as shown in the

TABLE I

GR-S POLYMERIZATION WITH SHARPLES TERTIARY OCTYL MERCAPTAN

Initial mercaptan concentration = 1.5 × 10^{-3} moles per 100 gm. monomers

Sample No.	Polymerization time, hr.	Conversion, %	Unreacted mercaptan, %	Solubility, %	Intrinsic viscosity, [η]
13 *A*	1	4.2	21	—	—
13 *B*	2	9.2	9.5	100	0.73
13 *C*	4	19.6	2.6	100	0.83
13 *D*	6	30.8	1.3	100	1.02
13 *E*	9	47.6	—	94	1.88
13 *F*	12	66.4	—	76	1.67

r = 13.7; k = 0.45; initial mercaptan loss = 64%.

TABLE II

GR-S POLYMERIZATION WITH SHARPLES TERTIARY DECYL MERCAPTAN

Initial mercaptan concentration = 1.5 × 10^{-3} moles per 100 gm. monomers

Sample No.	Polymerization time, hr.	Conversion, %	Unreacted mercaptan, %	Solubility, %	Intrinsic viscosity, [η]
16 *A*	2	9.7	45	100	0.79
16 *B*	4	22.8	27	100	0.98
16 *C*	6	34.8	17	100	1.18
16 *D*	9	54.8	3.7	100	1.75
16 *E*	12	70.8	1.1	100	2.44

r = 3.95; k = 0.175; initial mercaptan loss = 33%.

TABLE III

GR-S POLYMERIZATION WITH SHARPLES TERTIARY DODECYL MERCAPTAN

Sample No.	Polymerization time, hr.	Conversion, %	Unreacted mercaptan, %	Solubility, %	Intrinsic viscosity, [η]
Initial mercaptan concentration = 1.5 × 10^{-3} moles per 100 gm. monomers					
11 *A*	2	13.1	64	100	0.92
11 *B*	4	25.2	44	100	1.09
11 *C*	6	36.8	30	100	1.25
11 *D*	9	58.3	5.7	100	1.74
11 *E*	12	72.2	2.0	100	2.61
Initial mercaptan concentration = 3.0 × 10^{-3} moles per 100 gm. monomers					
12 *A*	2	12.9	61	100	0.55
12 *B*	4	26.8	40	100	0.58
12 *C*	6	39.2	27	100	0.66
12 *D*	9	59.6	6.2	100	0.81
12 *E*	12	74.1	1.1	100	1.15

r = 3.16; k = 0.02; initial mercaptan loss = 4.5%.

TABLE IV

GR-S POLYMERIZATION WITH SHARPLES TERTIARY HEXADECYL MERCAPTAN

Sample No.	Polymerization time, hr.	Conversion, %	Unreacted mercaptan, %	Solubility, %	Intrinsic viscosity, $[\eta]$
Initial mercaptan concentration = 1.5 × 10^{-3} moles per 100 gm. monomers					
14 *A*	2	13.3	91	11	—
14 *B*	4	23.4	87	15	—
14 *C*	6	32.5	82	16	—
14 *D*	9	52 8	75	17	—
14 *E*	12	70.6	53	18	—
14 *F*	15	79.8	39	32	—
Initial mercaptan concentration = 3.0 × 10^{-3} moles per 100 gm. monomers					
15 *A*	2	13.3	95	98.6	3.59
15 *B*	4	22.5	90	76	3.62
15 *C*	6	34.6	82	59	3.69
15 *D*	9	55.0	69	58	3.27
15 *E*	12	71.8	55	65	2.80
15 *F*	15	81.5	38	69	2.53
Initial mercaptan concentration = 5 × 10^{-3} moles per 100 gm. monomers					
17 *A*	2	12.2	94	100	2.34
17 *B*	4	23.4	88	100	2.59
17 *C*	6	37.2	81	100	3.01
17 *D*	9	53.9	73	100	2.40
17 *E*	12	66.7	64	100	2.25
17 *F*	18½	86.7	26	100	2.07

$r = 0.58$; $k = 0$; initial mercaptan loss = 0.

hexadecyl mercaptan runs (Table IV). Thus in increasing the time of polymerization from 12 to 18½ hr., the conversion was increased only from about 70 to 87%.

In Fig. 1 are shown the various curves obtained when the logarithm of the per cent unreacted mercaptan is plotted against the conversion. It is evident that the rate of disappearance of the dodecyl and hexadecyl mercaptan is independent of the initial concentration. Furthermore, with the exception of C_8, all the mercaptans show a straight line up to about 40% conversion, apparently following a first-order disappearance rate up to that point. Hence it is possible to calculate a regulating index, r, for these mercaptans, as shown at the foot of each table. It is interesting to note that in all the cases except that of the hexadecyl mercaptan the straight line obtained at low conversions

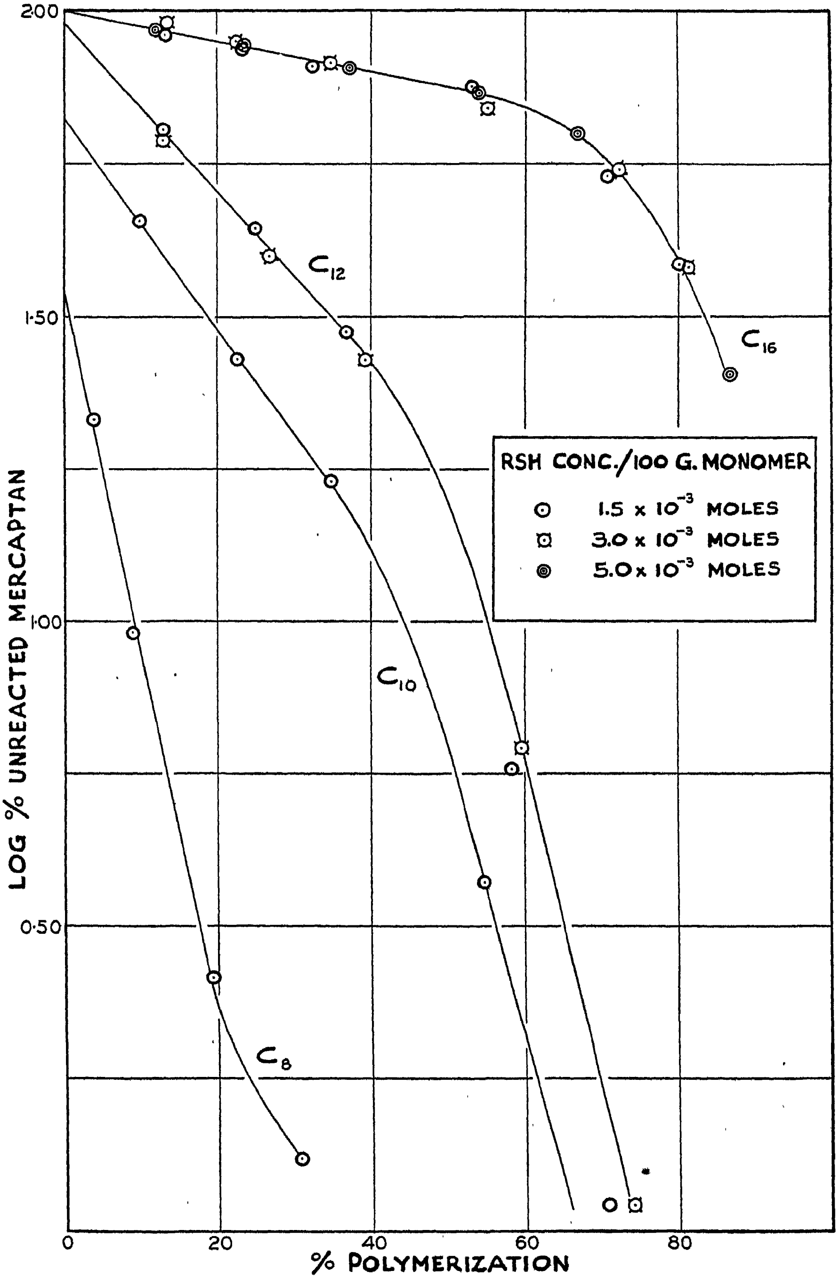

FIG. 1. *Rate of disappearance of various tertiary mercaptans.*

does not pass through the origin but has an intercept on the ordinate. Hence the equation of this straight line is expressed by

$$P = -\frac{2.3}{r}\log\frac{R}{R_0} - \frac{2.3\,k}{r} \tag{4}$$

$$= -\frac{2.3}{r}\left[\log\frac{R}{R_0} + k\right],$$

where P is fraction of polymer formed at any given time,

R is the concentration of mercaptan at that time,

R_0 is the initial concentration of mercaptan,

r is the regulating index,

k is a constant denoted by the intercept on the $\log\frac{R}{R_0}$ axis.

This equation differs somewhat from the original equation of Ewart *et al.*, where no account is taken of the intercept on the $\log\frac{R}{R_0}$ axis, thus,

$$P = -\frac{2.3}{r}\log\frac{R}{R_0}.$$

According to Kolthoff (7) the constant, k, represents the loss of mercaptan that occurs at the beginning of the polymerization by oxidation to disulphide. This loss, according to evidence presented by Kolthoff, is known to occur entirely in the very early stages of the polymerization reaction. Hence the straight lines obtained in plotting the logarithm of unreacted mercaptan against the conversion can, on this basis, be accepted as true indications of the disappearance of mercaptan by its modifying action. If, on the other hand, the mercaptan continues to undergo side-reactions during the course of the polymerization, then the straight line obtained may be merely fortuitous. No evidence on this point, other than that offered by Kolthoff, can be presented at the present time.

As can be seen, each mercaptan has a characteristic value for r and k. Thus the regulating index of the tertiary octyl mercaptan has the high value of 13.7 while that of the hexadecyl mercaptan has the low value of 0.58. The regulating indices of the decyl and dodecyl mercaptans are fairly similar, as shown by their values of 3.95 and 3.16, respectively. In other words, the octyl mercaptan is a very active modifier and hence disappears very rapidly, the decyl and dodecyl mercaptans are not as active as the octyl, and therefore disappear more slowly, whereas the hexadecyl mercaptan is much less active and consequently disappears much more slowly. On the basis of this line of reasoning, the octyl mercaptan should yield very low molecular weight polymer at the start of the polymerization, but the molecular weight of the polymer should increase rapidly owing to the sharp decline in the mercaptan concentration. In the same way, the relatively inactive hexadecyl mercaptan should give fairly high molecular weight polymer at the start of the polymerization, and its slower rate of disappearance should, therefore, not lead to any sharp increase in molecular weight of the polymer during the course of the polymerization. These considerations will be reviewed more fully in the light of the data on the characterization of the polymers obtained at various conversions.

The value of the constant, *k*, deserves some discussion. For the sake of convenience, this constant has been recalculated to show its true significance, i.e., the mercaptan loss at the very start of the polymerization. It can be seen that, on this basis, the octyl mercaptan experiences a loss of 64% of its initial concentration before it starts its modifying action, the decyl mercaptan shows an initial loss of 33%, the dodecyl mercaptan shows a much smaller loss of 4.5%, while the hexadecyl mercaptan shows no loss whatsoever. It is not surprising to see a correlation between the initial loss of these mercaptans and their rate of disappearance during polymerization, since these are both functions of the reactivity of the mercaptan in question.

From the above considerations it becomes apparent that the magnitude of the constant, *k*, will also affect the molecular weight of the polymer formed, since it alters the effective initial concentration of mercaptan. In other words, because a large proportion of the octyl mercaptan is postulated to disappear before it has an opportunity to act as a modifier, the initial concentration of this mercaptan is in actuality much less than expected.

Hence the molecular weight of the polymer formed at the start of such a polymerization should be somewhat higher than if the octyl mercaptan had not suffered such a depletion. Stating this in another way, the molecular weight of the polymer formed is a function both of the regulating index of the mercaptan and of its initial concentration. Hence the value of *k* should have an important effect on the molecular weight, inasmuch as it affects the real initial concentration of the mercaptan.

Solubility and Intrinsic Viscosity of Polymers

Data on the benzene solubility and the dilute solution viscosity of the various polymers obtained with different mercaptans and at different conversions are also shown in Tables I to IV, inclusive. It can be seen that at the concentrations used, the octyl, decyl, and dodecyl mercaptans yielded soluble polymer during the greater part of the polymerization The hexadecyl mercaptan, however, when present in a concentration of 3.0×10^{-3} moles per 100 gm. of monomer, or less, showed formation of insoluble polymer even in the early stages of the reaction. This is shown in Table IV. Here the intrinsic viscosities apply only to the soluble portion of each polymer, as would be expected. The results obtained with the use of a still lower concentration of hexadecyl mercaptan viz., 1.5×10^{-3} moles per 100 gm. of monomers, are not shown in the above tables, since the resulting polymers had a very low content of soluble material, much too low for any significant viscosity data. However, since it was considered of interest to note the variation in gel formation during the course of such a polymerization, the solubility values are shown separately in Table V.

The value for the intrinsic viscosity of each polymer was derived in the usual fashion, by extrapolating to zero concentration the straight line obtained

TABLE V

SOLUBILITY OF GR-S MODIFIED BY TERTIARY HEXADECYL MERCAPTAN

1.5×10^{-3} moles mercaptan per 100 gm. monomers

Sample No.	14 *A*	14 *B*	14 *C*	14 *D*	14 *E*	14 *F*
Conversion, %	13.3	23.4	32.5	52.8	70.6	79.8
Solubility, %	11	15	16	17	18	32
Wt. of gel/100 gm. monomers	12	20	27	44	58	54
Gel swelling index	12	15	17	20	28	158

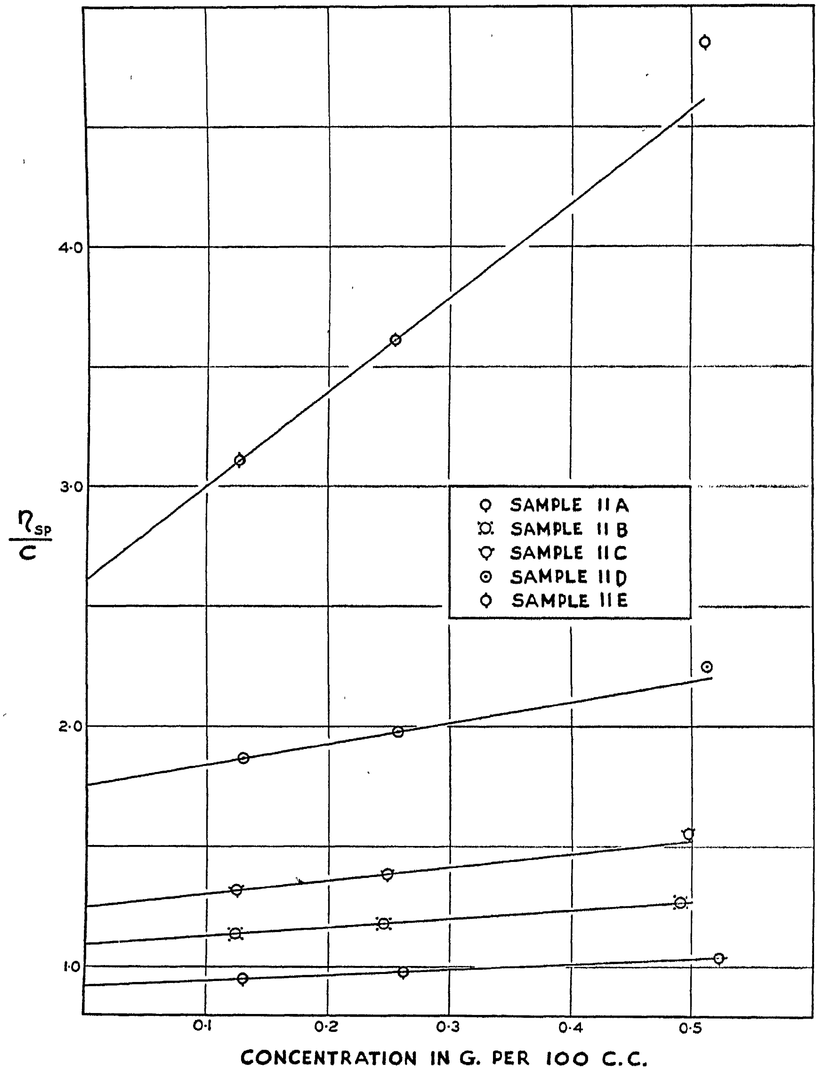

FIG. 2. *Viscosity–concentration curves of polymers modified by tertiary dodecyl mercaptan (1.5×10^{-3} moles per 100 gm. monomers).*

by plotting η_{sp}/c against c (9). A typical series of such lines is shown in Fig. 2. It may be noted that, although the polymers obtained at low conversions exhibit a good linearity between the three concentrations used, this is not so for the high conversion polymers. The latter have been found, in most cases, to yield viscosity–concentration curves having a definite concavity upwards that could not be accounted for by any experimental error. In those cases, it was assumed that the solutions of higher concentration deviated more markedly from ideality. Hence a straight line relation was assumed between the two lower concentrations, and the extrapolation carried out on that basis.

Table VI contains a summary of the relations between intrinsic viscosity, conversion, regulating index, and wastage factor of each mercaptan. The conversion figures are shown in whole numbers on the basis of the average rate of polymerization, i.e., 6% per hour during the first 12 hr. An examination of these figures shows just how each mercaptan affected the molecular size of the polymer formed. Thus the octyl mercaptan, which has a rapid rate of disappearance (high value of r), produced a polymer of relatively low molecular weight in the early stages of the polymerization; but the molecular weight of the polymer apparently increased quite rapidly during the later stages of the reaction until, at higher conversion, gel formation began owing to the depletion of modifier. It must be remembered that this mercaptan suffered a great loss by side-reaction during the very early stages of polymerization, hence its effective initial concentration was really much lower than expected. It may be assumed, therefore, that in the absence of this initial loss the intrinsic viscosity of the polymer formed at the start of the polymerization would have been much lower than indicated. This also helps

TABLE VI

INTRINSIC VISCOSITY – CONVERSION DATA ON GR-S POLYMERS USING VARIOUS MERCAPTANS

Conversion, %	Intrinsic viscosity of polymers				
	Octyl mercaptan, 1.5×10^{-3} moles per 100 gm. monomers	Decyl mercaptan, 1.5×10^{-3} moles per 100 gm. monomers	Dodecyl mercaptan		Hexadecyl mercaptan, 5.0×10^{-3} moles per 100 gm. monomers
			1.5×10^{-3} moles per 100 gm. monomers	3.0×10^{-3} moles per 100 gm. monomers	
12	0.73	0.79	0.92	0.55	2.34
24	0.83	0.98	1.09	0.58	2.59
36	1.02	1.18	1.25	0.66	3.01
54	1.88	1.75	1.74	0.81	2.40
72	—	2.44	2.61	1.15	2.25
86	—	—	—	—	2.07
Regulating index of mercaptan	13.7	3.95	3.16	3.16	0.58
Initial loss of mercaptan, %	64	33	4.5	4.5	0

to explain why the octyl mercaptan, with its high regulating index, did not produce initial polymer of very much lower viscosity than that produced by decyl or dodecyl mercaptan, when all had apparently the same initial concentration. If it were not for the extensive depletion of the octyl mercaptan at the start of the reaction, it would have been logical to expect a much greater modification of the polymer by this mercaptan as compared to the others.

This principle is demonstrated in a converse fashion in the case of the dodecyl mercaptan. Although its regulating index of 3.16 is considerably lower than that of the very active octyl mercaptan, it is still a relatively active modifier. Thus, when it was present in the usual concentration of 1.5×10^{-3} moles per 100 gm. monomers, its rate of disappearance caused a fairly rapid increase in the intrinsic viscosity of the polymer formed. However, when its initial concentration was doubled, then the intrinsic viscosity of the initial polymer was lowered considerably and the rate of increase in viscosity was much slower during the polymerization. Hence it can be seen that a modifier having a fairly high regulating index, when present in a low initial concentration, results in a polymer of great molecular heterogeneity at high conversions. If the same modifier is present in a larger initial concentration, then the resulting polymer will be more homogeneous at high conversions but the average molecular weight will be much lower. Thus a modifier with a regulating index of 3 or higher can produce either a very heterogeneous polymer of moderately high average molecular weight, or a more homogeneous polymer of much lower average molecular weight.

Although the question of the most favourable molecular weight and molecular weight distribution for synthetic rubber is still undecided, there is much indication that a polymer of high molecular weight and relative homogeneity is definitely desirable. It is obvious, then, that this can be achieved by using a modifier with a low regulating index in a suitable initial concentration to yield reasonably high molecular weight polymer at the start of the polymerization. Such a modifier would then cause only a slight increase in molecular weight during the polymerization, since its rate of disappearance would be quite slow.

In this connection, it is interesting to examine the results obtained in using the hexadecyl mercaptan at three different initial concentrations. This regulator is apparently too inactive to yield completely soluble polymer, when present in initial concentrations of 1.5×10^{-3} moles and 3.0×10^{-3} moles per 100 gm. of monomers. However, when the concentration was raised to 5.0×10^{-3} moles, completely soluble polymer was obtained at conversions up to 90%. From the intrinsic viscosities obtained using hexadecyl mercaptan at this concentration, it can be observed that the average molecular weight of the polymer showed a slow increase up to a conversion of about 40%, and then exhibited a somewhat sharper decline, which continued right up to about 90% conversion. This type of behaviour, i.e., a decreasing average molecular weight during part of the polymerization reaction, is quite different from anything encountered in the case of the other modifiers.

It may be readily noted that the increasing intrinsic viscosity occurred during that part of the polymerization reaction where the rate of disappearance of the hexadecyl mercaptan followed the first-order equation, i.e., up to 40% conversion. Thus the period during which the intrinsic viscosity decreased corresponds with the period during which the mercaptan disappearance curve showed a sharply increased rate. This phenomenon can be due to two possible mechanisms:

(1) Formation of lower molecular weight polymer during the later part of the polymerization reaction, due to an increased rate of disappearance of modifier, caused by some unknown factor.

(2) Formation of lower molecular weight polymer by interaction between the mercaptan and the polymer already present, i.e., by some mechanism of chain scission.

In this connection it is of great interest to examine the results shown in Table V. From the per cent solubility it can be seen that the total polymer, at any time during polymerization, showed an increasing solubility. This may again be due to two different effects, viz., either the formation of progressively more soluble polymer increments, or interaction between mercaptan and any insoluble polymer already formed. The calculation of the total weight of gel present per 100 gm. of original monomers is helpful in this case. It may be seen that the actual quantity of gel has suffered a reduction between the 12th and 15th hour of polymerization. In addition, it may be noted that the character of this gel has changed from that of a highly cross-linked structure ('tight gel') to that of a weakly cross-linked network ('Type A' gel), as indicated by the sharp rise in the gel swelling index. This evidence points to some bond scission reaction between the mercaptan and the gel.

It must be stated, however, that it is very probable that the rate of modification by the hexadecyl mercaptan is actually increased during the later part of the polymerization, aside from any polymer–mercaptan reaction. It is obvious that above 70% conversion, where the rate of polymerization begins to fall off, the rate of mercaptan disappearance should increase, since the original assumption of Ewart *et al.* no longer holds. However, it is equally apparent from Fig. 1 that the regulating activity begins to increase before this conversion is reached. Such an increased rate of regulating activity could possibly be due to the following effects:

(1) Change in the locus of reaction,

(2) Slow rate of solubilization of hexadecyl mercaptan,

(3) Change in butadiene–styrene ratio.

It is known that after 30 to 40% polymerization all the soap becomes adsorbed on the polymer particles and the locus of reaction shifts from the original soap micelles to the polymer particles themselves. Since this may favour an increased solubility of mercaptan it may also be the cause of an increased rate of disappearance of the mercaptan. As for the second factor mentioned above, it is known that the solubilization rate of tertiary hexadecyl mercaptan is markedly slower than that of the lower mercaptans. Hence it is possible that, during the later part of the polymerization, when the solubility of this mercaptan shows an increase, its rate of activity would also show an apparent increase. In other words, there would arise the double effect of an increased amount of solubilized mercaptan and a decreased concentration of monomer. This possibility cannot be ignored. It is also well known that the rate of entry of butadiene and styrene into the polymer is such as to lead to an accumulation of styrene so that the composition of the polymer formed after 50 or 60% conversion changes markedly toward higher styrene content. This change may have an effect in changing the rate of regulation. It is impossible at present to state definitely which of the above factors is responsible for the anomalous behaviour of hexadecyl mercaptan during the later stages of the polymerization reaction, but it is hoped that further work will help to elucidate the mechanism.

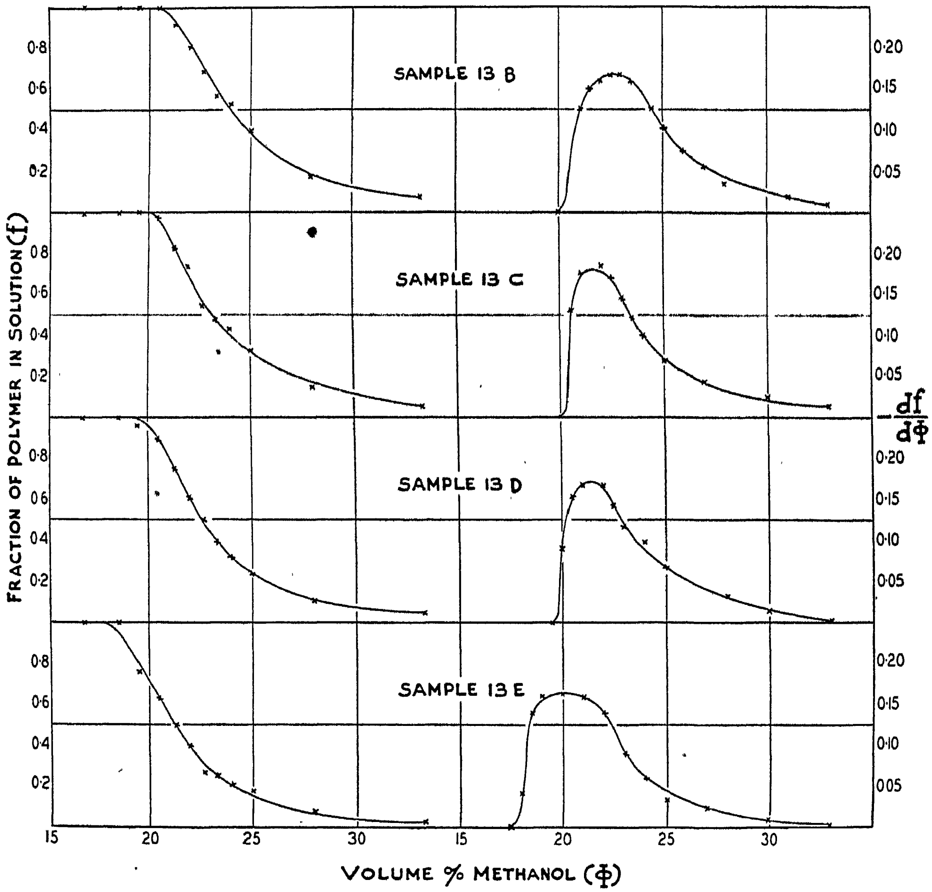

FIG. 3. *Precipitation distribution functions for polymers modified by tertiary octyl mercaptan (1.5 × 10^{-3} moles per 100 gm. monomers).*

Precipitation Distribution Functions of Polymers

The precipitation distribution functions obtained for all the completely soluble polymers are shown in Figs. 3 to 7. The solubility curves were drawn in such a fashion as to best fit the experimental points, while the distribution curves were then plotted by determining the change in slope of the solubility curves during precipitation. In this way a smooth continuous function was obtained.

It is evident from a general examination of all the precipitation distribution curves that the polymers became more molecularly heterogeneous during the

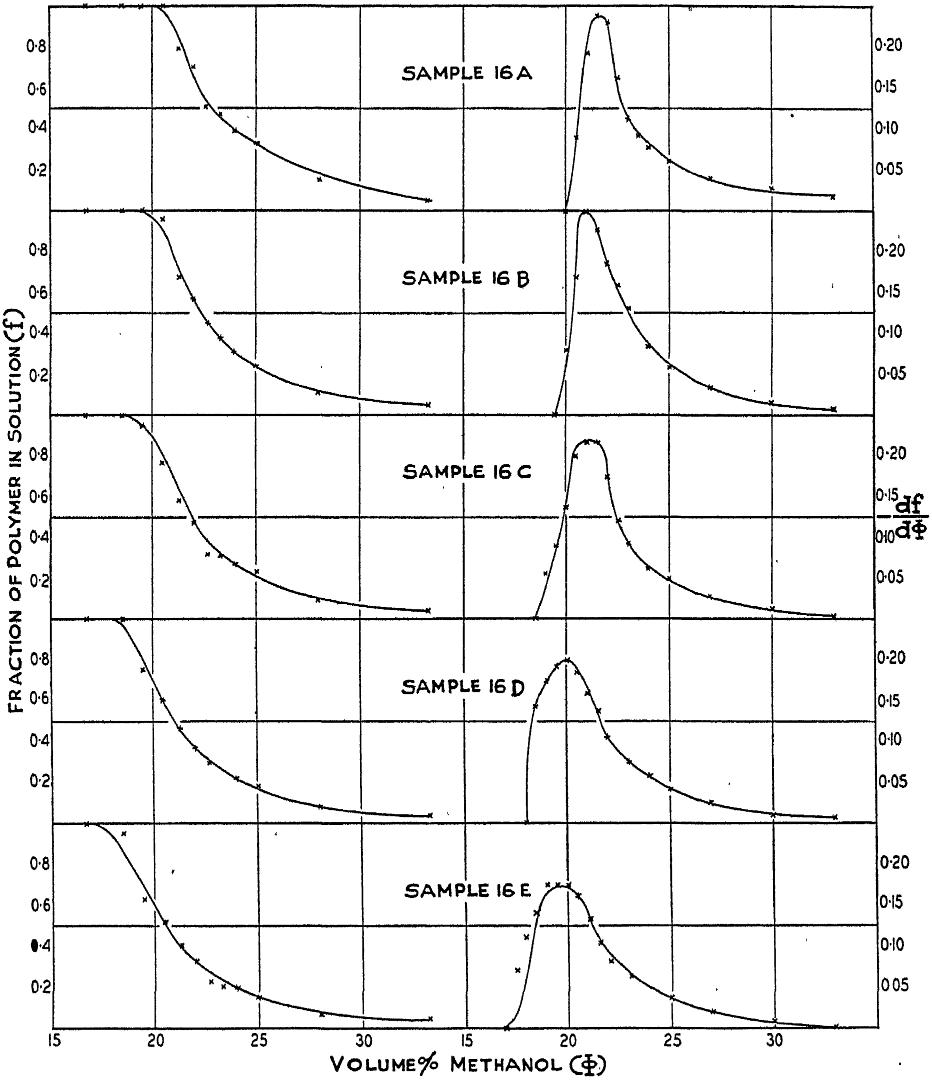

FIG. 4. *Precipitation distribution functions for polymers modified by tertiary decyl mercaptan (1.5 × 10^{-3} moles per 100 gm. monomers).*

course of the polymerization. However, it must be borne in mind that these curves do not necessarily represent an accurate quantitative measure of the molecular heterogeneity. Thus it can be seen that all the polymers showed a long 'tail' in the direction of the lower molecular weights and a much more abrupt slope at higher molecular weights. This is very likely an exaggerated effect caused by the high solubility of the lower molecular weight material as compared to that of the higher molecular weight polymer, and need not represent a true molecular weight distribution. From a consideration of the kinetics of addition polymerization, and from data obtained by careful

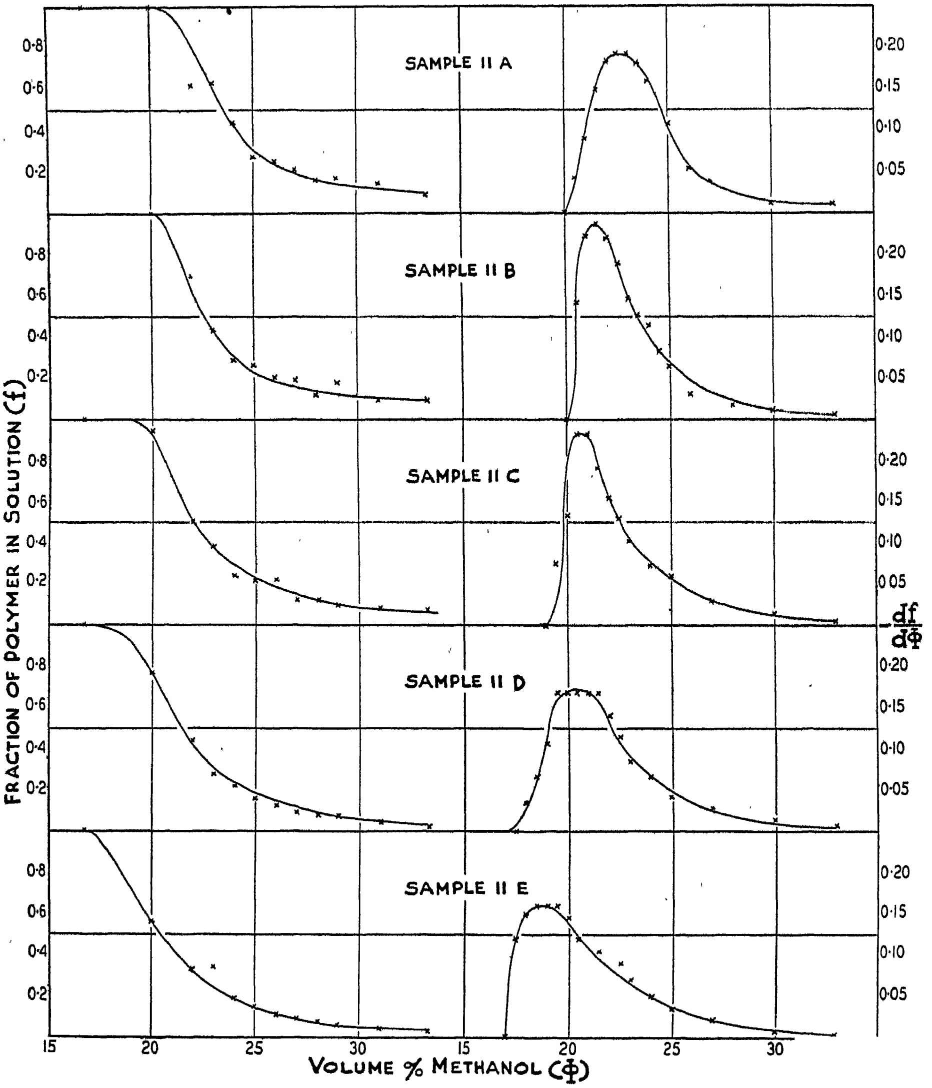

FIG. 5. *Precipitation distribution functions for polymers modified by tertiary dodecyl mercaptan (1.5 × 10^{-3} moles per 100 gm. monomers).*

fractionation studies, it has been shown that the molecular weight distribution of this type of polymer generally exhibits an abrupt rise in the low molecular weight region and an extended slope in the high molecular weight region. This is the exact reverse of the type of distribution curve shown in Figs. 3 to 7, inclusive, since increasing values of the volume per cent methanol (Φ) represent the precipitation of polymer having decreasing values of molecular weight. The fact that these precipitations were carried out with the use of only 12 precipitant solutions undoubtedly helps to decrease the accuracy of the curves. Furthermore, Flory (5) recently pointed out that in any fractionation of a

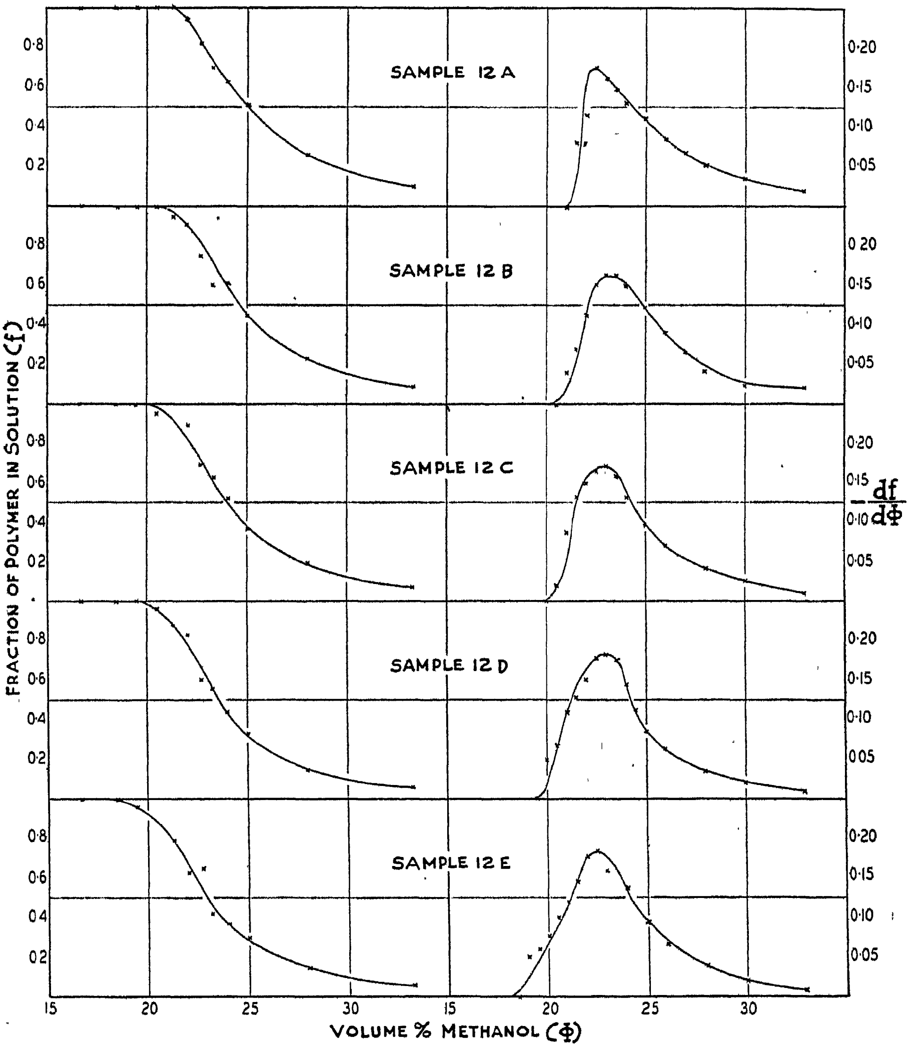

FIG. 6. *Precipitation distribution functions for polymers modified by tertiary dodecyl mercaptan (3×10^{-3} moles per 100 gm. monomers).*

polymer solution due consideration must be given to the great differences in solubility of high and of low molecular weight material, and that this must be done by adjusting the concentration of the solution for each molecular species.

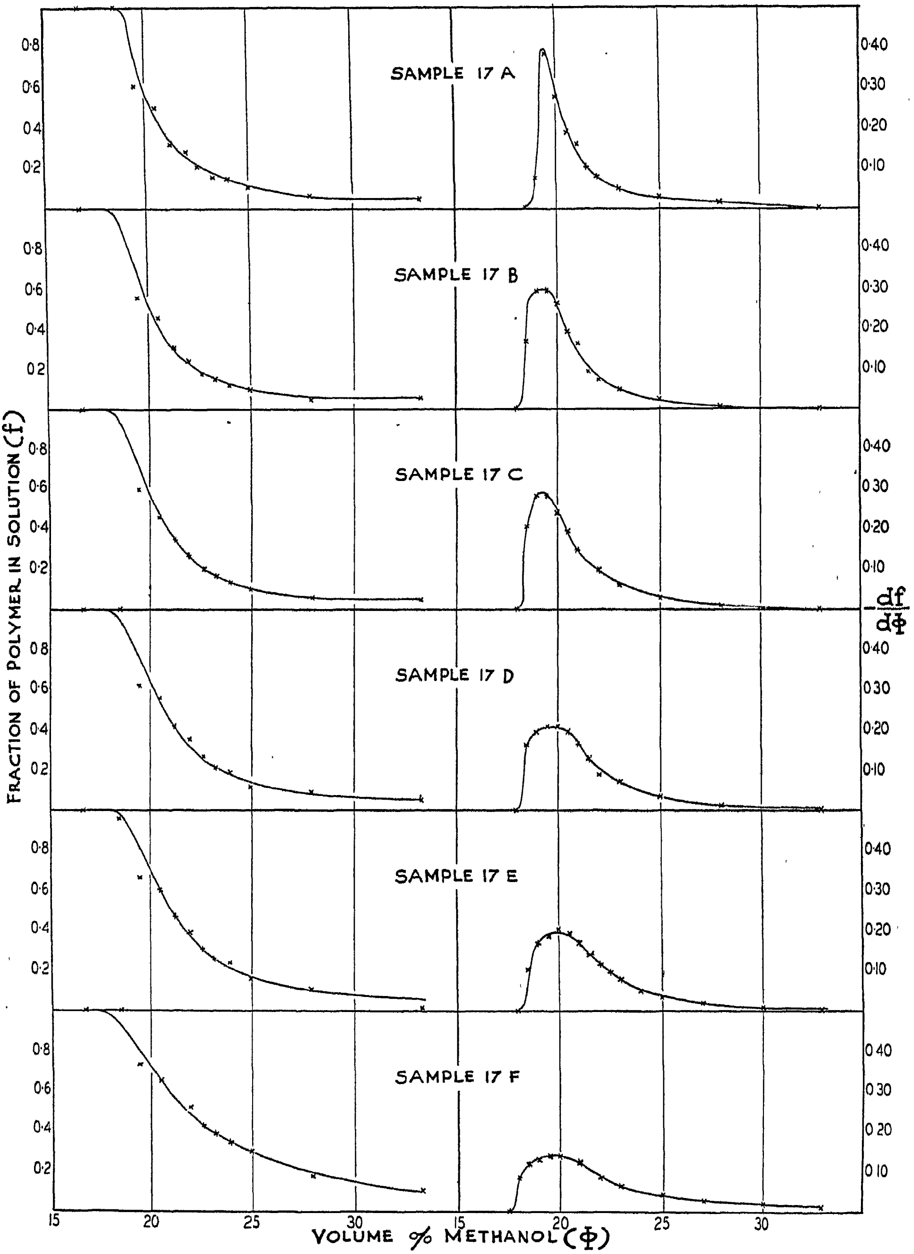

FIG. 7. *Precipitation distribution functions for polymers modified by tertiary hexadecyl mercaptan (5 × 10^{-3} moles per 100 gm. monomers).*

However, it can be said that the precipitation curves shown here still represent at least a qualitative picture of the molecular homogeneity of the polymers under consideration.

Although all the distribution curves undergo a shift towards higher molecular weights (lower Φ values) and, at the same time, show a wider spread, denoting increased heterogeneity, they do so in varying degrees. Thus it can be seen that the polymers modified by decyl mercaptan (Fig. 4) and dodecyl mercaptan (Fig. 5) show approximately the same degree of heterogeneity and the same change in heterogeneity during the polymerization, when both mercaptans are present in the same concentration. However, when the dodecyl mercaptan is used in a higher concentration (Fig. 6) the change in heterogeneity is not as great during the course of the polymerization. This is in agreement with the previous discussion on the relation between the regulating index and intrinsic viscosity.

Another illustration confirming the previous discussion can be seen in the curves of the polymers modified by octyl mercaptan. Here it would be expected that the change in heterogeneity would be marked during the course of the reaction, since this mercaptan has a high rate of disappearance, i.e., low molecular weight polymer should be formed at the start of the polymerization and very high molecular weight polymer during the later stages. However, it has already been noted that a large proportion of this mercaptan disappears by a side-reaction at the very start of the polymerization, hence the effective concentration is reduced drastically and thus the polymer produced initially is not as low in molecular weight as would be expected. Hence the distribution curves, as shown, do not indicate a drastic change in heterogeneity with increasing conversion. Instead they show a relatively moderate increase in heterogeneity as well as the expected shift toward higher molecular weight.

The distribution curves obtained in the case of the GR-S modified by hexadecyl mercaptan (Fig. 7) show perhaps the most interesting changes. It should be remembered that the ordinates here have been drawn to half-scale, compared to the ordinates used for all the other curves. Hence the height of each distribution curve should be doubled, for a comparison with the other polymers. The most striking feature in this series of curves is the marked increase in heterogeneity during the course of the polymerization. This increase in heterogeneity is apparently accomplished by a simultaneous increase in both the higher and lower molecular weight fractions. It can be seen that up to 40% conversion (Samples 17*A*, 17*B*, and 17*C*) there is a definite shift towards the higher molecular weights, the amount of lower molecular weight material remaining relatively constant. However, during the latter part of the polymerization (Samples 17*D*, 17*E*, 17*F*) there appears to be a definite shift towards both the higher and the lower molecular weights, resulting in a flattening and broadening of the distribution curve. This seems to confirm the postulate that there is an interaction between polymer molecules and mercaptan, occurring during the later stages of the polymerization, which leads to the formation of lower molecular weight material at the same time as the usual chain transfer reaction continues to form higher molecular weight polymer.

Thus it may be seen that these precipitation distribution curves offer at least qualitative evidence corroborating the evidence obtained from the data on mercaptan disappearance and intrinsic viscosities. In addition, the curves for the polymers modified by hexadecyl mercaptan offer new evidence for the postulated polymer–mercaptan reaction previously advanced.

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THE EQUILIBRIUM DIAGRAMS AND CRYSTALLIZATION VELOCITIES OF THE SYSTEMS: (*a*) PICRIC ACID – 2,4-DINITROPHENOL; (*b*) DINITROPHENOL – TRINITROTOLUENE; (*c*) PICRIC ACID – DINITROPHENOL – TRINITROTOLUENE[1]

By A. N. Campbell[2] and E. J. Pritchard[3]

Abstract

The equilibrium diagrams of the systems: picric acid – 2,4-dinitrophenol, trinitrotoluene – 2,4-dinitrophenol, and picric acid – dinitrophenol – trinitrotoluene have been determined.

As this investigation was carried out to find the suitability of various mixtures for shell filling, the densities of a number of liquid mixtures of the above components were determined. For the same reason, viscosities and crystallization velocities were investigated.

The crystallization velocities were far from additive, the crystallization velocity of a mixture being less than that of either of the components. Tammann's type of curve, in which the velocity of crystallization attains a constant value after a certain degree of supercooling, was not obtained, but a maximum crystallization velocity resulted, in most cases, at about 20° to 30° C. of supercooling. Comparison of viscosity and crystallization velocity shows that a direct relation does not exist, but increase of viscosity at constant temperature does always reduce the crystallization velocity.

Addition of guncotton increased the viscosity of Shellite considerably without producing much effect on the crystallization velocity. The addition of a crystalline third component lowered both the melting point and the crystallization velocity.

Introduction*

Picric acid by itself is a violent explosive, but the pure material melts at too high a temperature (122° C.) for convenient shell filling, 105° C. being the maximum temperature permissible. It is also rather sensitive. By the addition of 2,4-dinitrophenol, the melting point of the mixture is lowered below the above maximum, and this addition also renders it much less sensitive.

During the first World War, Italy and France (6, pp. 78, 174) used a mixture of picric acid and dinitrophenol in the proportions: 65% picric acid and 35% dinitrophenol. Great Britain used a similar mixture, called 'Shellite', consisting of 60% picric acid and 40% dinitrophenol.

Although Shellite was an improvement on pure picric acid, from the point of view of shell filling, it was not completely satisfactory, because of the large amount of shrinkage on solidification. The idea was therefore put forward, by Dr. Wright of Toronto University, that the amount of cavitation might be reduced if it were possible to cool the melt to room temperature, before crystallization set in. The shrinkage would thus be from the top downwards, and a further charge could then be added. The problem therefore was that of retaining Shellite in the vitreous condition, at least for a time, after it had cooled to room temperature. It has been shown by one of us (A.N.C.) (3), that, while it seems impossible to prevent the spontaneous formation of nuclei, their velocity of growth can readily be decreased by increasing the viscosity of the medium.

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Contribution from the Department of Chemistry, University of Manitoba, Winnipeg, Man.

[2] *Professor of Chemistry and Head of Department.*

[2] *Holder of a Bursary under the National Research Council of Canada, 1942–1943.*

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A systematic investigation was therefore carried out on the following characteristics of the systems mentioned in the title:

1. Equilibrium diagrams,
2. Densities of liquid mixtures at 130° C.,
3. Viscosities of liquid mixtures at 130° C.,
4. Velocities of crystallization of the pure substances and of the eutectic mixtures with increasing degrees of supercooling.

After the above data were obtained, the experiments were repeated using various addition agents to increase the viscosity and decrease the velocity of crystallization.

Previous Work on Crystallization Velocity

The literature of this subject is fairly extensive and probably fairly well known. It is sufficient to say that the classical theory of the crystallization velocity of a supercooled liquid is that of Tammann (12). According to this theory, after a certain, and rather small, degree of supercooling, the temperature prevailing at the crystallizing boundary is always the melting temperature, independent of the degree of supercooling. In accordance with this, Tammann found experimentally that the velocity of crystallization increased rapidly with degree of supercooling, to attain a constant maximum, over a large range of supercooling: this maximum value again decreased for very great degrees of supercooling. More recently, in 1929, doubt has been cast on Tammann's theory. By direct measurement, and by mathematical treatment, Pollatschek (7) showed that the temperature prevailing at the boundary, solid–supercooled liquid, was never that of the melting point. In accordance with this and Pollatschek's own results for crystallization velocity, it would appear that the velocity of crystallization should attain a maximum value and then immediately decrease, without the existence of a region of constant crystallization velocity. Our results are in agreement with this finding.

Experimental Technique

The techniques of thermometry, viscosimetry, and density are too well known to require any description. The apparatus for determining velocity of crystallization was made from thick-walled hard glass capillary of 1 to 2 mm. internal diameter. It was bent in the standard U-shape, and one arm extended into wide glass tubing to facilitate filling, and inoculation of the supercooled liquid. The length of each arm was about 12 cm. A cathetometer was used to measure the distance crystallization had progressed downwards, in one arm, during a given time.

The first measurements of crystallization velocity were obtained by noting the time taken for crystallization to progress from one mark on the side tube to another, 10 cm. distant. This is satisfactory if spontaneous crystallization does not take place. When spontaneous crystallization does take place, it was found more satisfactory to follow the progress of crystallization from one spontaneously induced nucleus by means of the cathetometer: most of the measurements were done this way.

The determinations of equilibrium diagrams were made by two methods, viz., that of thermal analysis, accompanied whenever possible by the visual observation of the temperatures at which crystals appeared, and by the thaw point-melting point method (8, 9, 10, 11). About the former method nothing need be said, but something should be said of the latter, because it has in the opinion of the authors been somewhat neglected. The method consists simply in observing, in any melting point apparatus, the temperature at which a given mixture begins to 'thaw', i.e., to appear moist, and the temperature of complete melting, i.e., the temperature at which the last crystal skeleton disappears. In this way a complete knowledge of solidus and liquidus curves is obtained. The method requires some practice in its use, but it has the advantages that it is a semi-micro method and therefore is particularly applicable to the study of explosives and of rare and expensive substances, and, also, it occasionally gives information that cannot be obtained by the method of thermal analysis. It is also notable that the method is quite independent of supercooling, the bugbear of thermal analysis when applied to organic systems.

The drawback to the method is the necessity for very pure materials. Slight impurity causes the thaw point line to run much below the true eutectic. In this respect the method of thermal analysis does not suffer so much from slight impurity. The materials of this investigation were almost invariably commercial materials, which were not purified, and hence the results are not in agreement as regards eutectic temperatures. This criticism, however, does not apply to the determination of melting point, at least not in our technique where the rate of heating was only 1° C. in three minutes: the danger of overrunning the melting point was therefore negligible.

We used a specially designed furnace for the thaw point-melting point method, consisting of a heavy cylinder of brass with a central opening for the thermometer and melting point tube. At right angles to this central opening and at 45° to each other, two holes were drilled in the side of the cylinder. One of these served to illuminate the melting point tube, the other for observation. The source of light and a magnifiying glass to facilitate observation were mounted on the same stand. The brass cylinder was wound with two layers of nichrome wire, suitably insulated and connected in series. The temperature was controlled by means of rheostats in series with the heating circuit. To ensure accuracy, when using the thaw point – melting point method, the temperature should not be raised more rapidly than one degree in three minutes.

Temperatures were measured by means of standardized mercury-in-glass thermometers, but were not corrected for exposed stem. All temperatures are given in degrees Centigrade. To avoid the frequent use of the lengthy names, trinitrotoluene and dinitrophenol, these are frequently abbreviated to T.N.T. and D.N.P. respectively.

Purity of Materials

The materials used throughout were the products of the explosives industry, without further purification. This was done deliberately, since the results of the investigation were intended to apply to the commercial products, and not to chemically pure material. Judging from the melting points, however, it seems that these products are not very seriously impure.

Results

EQUILIBRIUM DIAGRAMS

1. Picric Acid – 2,4-Dinitrophenol

This system has been investigated by Bogojawlenski (2), but since the original paper was not available, we thought it advisable to redetermine the diagram. This was done both by the thaw point – melting point method and by the method of thermal analysis. The results are contained in Tables I and II (*a*). In Table II (*b*) Bogojawlenski's results are compared with ours.

TABLE I

EQUILIBRIUM DATA OF THE SYSTEM: PICRIC ACID – DINITROPHENOL, BY THE THAW POINT – MELTING POINT METHOD

Composition, % picric acid	Softening point, °C.	Melting point, °C.
0.0	109.0	111.5
10.0	73.7	108.0
20.0	74.8	103.2
33.4	75.0	95.6
39.6	72.5	92.7
40.4	76.2	91.6
51.1	73.1	86.7
60.0	—	82.0
60.5	74.4	82.5
61.5	75.4	83.7
69.6	74.2	93.4
80.2	72.5	105.5
88.5	72.3	111.5
100.0	119.0	121.0

2. The System: Trinitrotoluene – 2,4-Dinitrophenol

This system was investigated by the method of thermal analysis only. The results are contained in Table III.

TABLE II (*a*)

EQUILIBRIUM DATA OF THE SYSTEM: PICRIC ACID – DINITROPHENOL, BY THE METHOD OF THERMAL ANALYSIS

Composition, % picric acid	Eutectic halt, °C.	Freezing point, °C.
0.0	—	111.9
10.0	—	107.3
20.0	—	102.0
30.0	78.4	95.9
40.0	78.5	88.0
40.0	79.3	90.2
50.0	78.6	81.0
50.0	78.8	80.9
55.0	79.2	—
60.0	79.0	80.8
70.0	79.1	92.5
80.0	—	102.4
90.0	—	111.7
100.0	—	120.7

TABLE II (*b*)

THE EUTECTIC TEMPERATURE AND COMPOSITION OF THE SYSTEM: PICRIC ACID – DINITROPHENOL

Observer	Method	Melting point of eutectic, °C.	Composition, wt. % picric acid
Bogojawlenski	?	81.5	57.9
Campbell and Pritchard	Thaw point, etc.	74.0 (observed) 81.0 (from intersection of liquidus curves)	59.0
Campbell and Pritchard	Thermal analysis	79.3	56.5

3. *Picric Acid – Trinitrotoluene*

This system was not investigated by us, but a knowledge of it is necessary, prior to the investigation of the ternary system: picric acid – dinitrophenol – trinitrotoluene. The system had already been investigated by Taylor and Rinkenbach (13) and by Giua (5). On plotting the results of both authors, those of Taylor and Rinkenbach seem more consistent. We therefore deduced the eutectic composition and temperature from their results as 34% picric acid and 59.8° C.

4. *The Systems: Picric Acid – Guncotton, and Dinitrophenol – Guncotton*

The melting points of various mixtures are given in Table IV. The guncotton was incorporated in the dinitrophenol by heating it with the molten dinitrophenol for one hour at 130° C. After this time, no guncotton was detectable in the 1% mixture under the polarizing microscope, but guncotton was still present in the form of threads in the 10% mixture. In making the guncotton – picric acid mixture, the required quantities were dissolved in acetone to secure a homogeneous mixture. The acetone was then evaporated off, and the resulting mixture heated at 130° C. for one hour to get rid of as much acetone as possible. Although all the acetone should come off above its boiling point (56° C.), it seems to be held by the viscous guncotton solutions.

TABLE III

THE SYSTEM: TRINITROTOLUENE – DINITROPHENOL, BY THE METHOD OF THERMAL ANALYSIS

Composition, % D.N.P.	Eutectic halt, °C.	Freezing point, °C.
0.0	—	80.1
10.0	—	74.2
20.0	62.4	67.7
30.0	62.7	64.0
40.0	62.7	73.7 73.4
50.0	—	84.3 83.6
50.0	—	84.7
60.0	—	91.4 91.2
70.0	—	97.4 97.1
80.0	—	102.6 102.1
90.0	—	107.0
100.0	—	111.2

TABLE IV

THE EFFECT OF GUNCOTTON ON THE MELTING POINT

Composition	Melting point, °C.
D.N.P. alone	111.5
D.N.P. + 1% guncotton	112.0–112.5
D.N.P. + 10% guncotton	112.0
Picric acid alone	120.5–121.0
Picric + 5% guncotton	118–122

NOTE:—*The viscosity of the mixtures prevented accurate determinations, but it was concluded that in the concentrations of guncotton that were used there was no measurable effect.*

5. *The System: Picric Acid – Dinitrophenol – Trinitrotoluene*

The approximate ternary eutectic composition of this system was found by assuming that the binary eutectic troughs were straight and could be represented by drawing straight lines from one pure component to the opposite binary eutectic. The three lines thus drawn met in a small triangle. The mixtures corresponding to the angular points of this triangle were then prepared and investigated both by the thaw point – melting point method and the method of thermal analysis. It was found, however, that owing to the exceedingly slow growth of the crystals, the heat effect was too slowly developed to permit of the use of the latter method in its true form: instead the temperature at which crystals were first visually detectable was taken. Presumably the lowest melting of these mixtures is nearest to the ternary eutectic, but none of the three melted in a homogeneous manner. Several more mixtures in this neighbourhood were prepared, but we never obtained a mixture that melted and froze at single temperature. We considered, however, that we approached close enough to it for the exigencies of war work. All the values obtained are collected in Table V.

TABLE V

THE SYSTEM: PICRIC ACID – DINITROPHENOL – TRINITROTOLUENE

No.	Composition, wt. %			Eutectic melting, °C.	Complete melting, °C.
	Picric acid	T.N.T.	D.N.P.		
1	28	50	22	45.4	52.5
2	29	51	20	45.7 - 47.0	49.2
		Same		40.6?*	46.8
3	27	52.5	20.5	45.6	49.5
4	31	56	13	—	52.5
5	30	55	15	—	49.3
6	30	53	17	—	48.5
7	27	55	18	—	49.5
8	32	52	16	—	51.0

* *Thermal analysis for comparison.*

NOTE:—*The composition of the ternary was taken as that of No. 6: 30% picric acid, 53% trinitrotoluene, and 17% dinitrophenol. The true ternary temperature was taken as 45° to 46° C., not 48.5° C.*

6. *Densities*

The densities of the complete system: picric acid – dinitrophenol at 130° C. are given in Table VI (*a*) along with the equation deduced from the data by the method of averages. In Table VI (*b*), (*c*), (*d*), the densities of various other mixtures are given, determined at temperatures approximately 10° C. above the melting point. The latter data were used in the calculation of viscosities.

7. *Viscosities*

The viscosity and fluidity (=1/viscosity) for the system picric acid – dinitrophenol were determined and the results are given in Table VII (*a*).

TABLE VI (*a*)

DENSITY OF THE SYSTEM: PICRIC ACID – DINITROPHENOL, AT 130° C.

Composition, % picric	Density, gm./cc.	Composition, % picric	Density, gm./cc.
0.00	1.45	47.20	1.51
6.49	1.46	61.60	1.53
14.63	1.46	74.06	1.56
19.92	1.47	81.50	1.57
26.50	1.48	91.55	1.60
40.36	1.50	100.00	1.61

NOTE:—*The equation deduced from the above, by the method of averages is:*

$$D_4^{130} = 1.445 + 1.078 \times 10^{-3}p + 6.24 \times 10^{-6}p^2,$$

where D = the density, and p = weight % picric acid.

TABLE VI (*b*), (*c*), (*d*)

(*b*) Density of some mixtures of the system of Table VI (*a*) at 90° C.

Composition, % picric acid	60	55	55% plus 5% guncotton
Density, gm./cc.	1.58	1.54	1.54

(*c*) Eutectic composition of T.N.T. – D.N.P. (28% D.N.P.)

Temperature, °C., 72.8 Density, 1.47

(*d*) Density of the ternary eutectic: picric acid – D.N.P. – T.N.T.

Temperature, °C.	56.0	26.0
Density	1.54	1.56

TABLE VII (*a*)

VISCOSITY OF THE SYSTEM: PICRIC ACID–DINITROPHENOL AT 130° C.

Composition		Viscosity, centipoises	Fluidity = 1/viscosity
Wt. % picric acid	Mole % picric acid		
0.0	0.0	2.64	0.379
10.0	8.19	2.93	0.342
20.0	16.72	3.22	0.311
30.0	25.62	3.71	0.269
40.0	34.90	4.25	0.235
50.0	44.54	4.85	0.206
60.0	54.64	5.73	0.175
70.0	65.21	6.74	0.148
80.0	76.20	8.04	0.124
90.0	87.80	9.68	0.103
100.0	100.0	11.78	0.085

The viscosities of various mixtures at various temperatures are given in Table VII (*b*). In Table VII (*c*) the viscosities of the ternary eutectic for different degrees of supercooling are given.

TABLE VII (*b*)

System	Composition	Temperature, °C.	Viscosity, centipoises
Picric acid–D.N.P.	60% picric acid	90	17.96
Picric acid–D.N.P.	55% picric acid	90	15.14
Picric acid–D.N.P.	55% + 1% guncotton	90	113.7
Picric acid–D.N.P.	55% + 5% guncotton	90	Acts like glue
T.N.T.–D.N.P.	28% D.N.P.	72.8	12.96

TABLE VII (*c*)

VISCOSITY OF TERNARY EUTECTIC: PICRIC ACID – DINITROPHENOL – TRINITROTOLUENE FROM APPROXIMATELY 10 DEGREES ABOVE TO 20 DEGREES BELOW ITS MELTING POINT

Temperature, °C.	Viscosity, centipoises	Temperature, °C.	Viscosity, centipoises
56	49.3	36	180.2
51	67.4	31	290.0
46	86.5	26	470.0
41	124.2		

8. *Velocity of Crystallization*

Owing to spontaneous crystallization, it was found impossible to follow the velocity of crystallization of pure picric acid and pure dinitrophenol to many degrees of supercooling. The results obtained, however, agree closely with those of Bogojawlensky (1). These are given in Table VIII (*a*) and are plotted in Fig. 1.

The crystallization velocity of trinitrotoluene had not previously been determined. By following one spontaneously induced nucleus with a cathetometer, it was found possible to extend the measurements to room temperature. The results are given in Table VIII (*b*) and are plotted in Fig. 1.

The crystallization velocity of a 60% picric acid – 40% dinitrophenol mixture is given in Table VIII (*c*), and that of 55% picric acid, with 0, 1, and 3% added guncotton, is given in Table VIII (*d*), and plotted in Fig. 2, Curves I, II, and III respectively. The velocity of crystallization of the eutectic mixture in the system dinitrophenol-trinitrotoluene is given in Table VIII (*e*), while the values for the ternary eutectic are given in Table VIII (*f*). The curves of Fig. 3 refer to:— A. 60% picric acid, 40% dinitrophenol; B. 28% dinitrophenol, 72% trinitrotoluene; C. 55% picric acid, 45% dinitrophenol; D. the ternary eutectic. Curve *C* of Fig. 3 and Curve I of Fig. 2 are the same curve.

TABLE VIII (*a*)

VELOCITY OF CRYSTALLIZATION OF PICRIC ACID AND 2,4-DINITROPHENOL

Temperature, °C.	Degrees of supercooling	Velocity, mm./min.	
		Bogojawlensky	Pritchard
Picric acid			
110	12	343	366 ± 18
100	22	681	
95	27	783	
90	32	811	
85	37	858	
80	42	858	
Dinitrophenol			
100	12.8	6.35	7.52
90	22.8	16.2	18.0
80	32.8	30.3	35.4
70	42.8	55.7	
60	52.8	76.8	
50	62.8	83.2	
40	72.8	88.3	

NOTE:—*The above values are plotted in Fig. 1.*

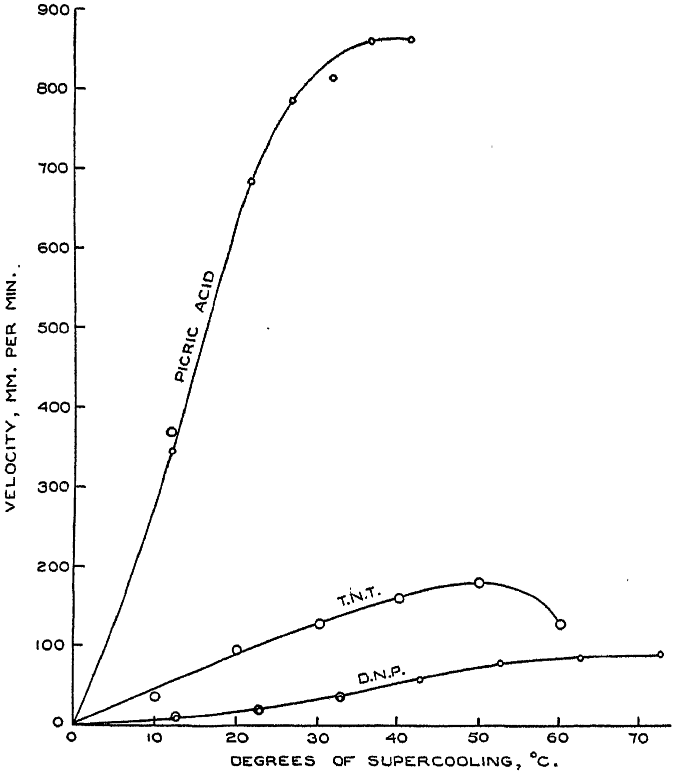

FIG. 1. *Velocity of crystallization.* o—*A. Bogojawlensky's results.* O—*E. Pritchard's results.*

TABLE VIII (*b*)

CRYSTALLIZATION VELOCITIES OF TRINITROTOLUENE

Temperature, °C.	Degrees of supercooling	Velocity, mm./min.
22.0	58.1	127
30.0	50.1	171
40.0	40.1	158
50.0	30.1	126
60.0	20.1	94
70.0	10.1	35

NOTE:—*These values are also plotted in Fig. 1.*

TABLE VIII (*c*)

CRYSTALLIZATION VELOCITY OF THE SYSTEM: 60% PICRIC ACID – 40% DINITROPHENOL (SEE FIG. 3, CURVE *A*)

Temperature, °C.	Degrees of supercooling	Velocity, mm./min.
70	9.3	1.28
60	19.3	2.05
50	29.3	1.89
40	39.3	1.02
30	49.3	0.47
20	59.3	0.14
13	66.3	0.075

TABLE VIII (*d*)

CRYSTALLIZATION VELOCITIES OF THE SYSTEM: 55% PICRIC ACID – 45% DINITROPHENOL WITH ADDED GUNCOTTON (SEE FIG. 2 AND FIG. 3, CURVE *C*)

Temperature, °C.	Degrees of supercooling	Velocity, mm./min.		
		0% guncotton. Curve I	1% guncotton. Curve II	3% guncotton. Curve III
70	9.3	0.09	0.20	0.11
60	19.3	0.37	0.64	0.30
50	29.3	0.54	0.69	0.34
40	39.3	0.43	0.44*	0.22
30	49.3	0.23	0.38	0.13
21	58.3	0.09	0.21	0.05

* *Not plotted.*

TABLE VIII (*e*)

CRYSTALLIZATION VELOCITIES OF THE SYSTEM: 28% DINITROPHENOL - 72% TRINITROTOLUENE (SEE FIG. 3, CURVE *B*)

Temperature,° C.	Degrees of supercooling	Velocity, mm./min.
60	2.7	0.13
50	12.7	0.77
40	22.7	1.76
30	32.7	1.81

TABLE VIII (*f*)

CRYSTALLIZATION VELOCITIES OF THE TERNARY EUTECTIC: PICRIC ACID – DINITROPHENOL – TRINITROTOLUENE (SEE FIG. 3, CURVE *D*)

Temperature, °C.	Degrees supercooling	Velocity, mm./min.
36	10	0.051
26	20	0.052
0	46	0.014

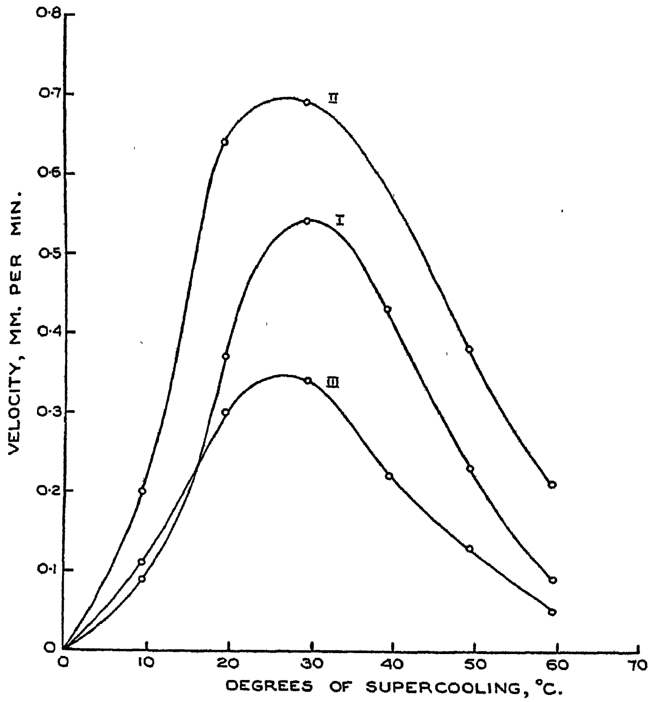

FIG. 2. *Effect on the velocity of crystallization of adding guncotton to the eutectic composition. I—Eutectic alone. II—Eutectic plus 1% guncotton. III—Eutectic plus 3% guncotton.*

Discussion of Results

EQUILIBRIUM DIAGRAMS

The System: Picric Acid – 2,4-Dinitrophenol

Owing to the discrepancy between the results obtained for the eutectic by the two methods, no definite composition can be deduced for it. It seems, however, that the composition should be closer to 60% picric acid than 50% because the crystallization velocity of dinitrophenol is very much less than that of picric acid and therefore the method of thermal analysis tends to give results that are too low on the dinitrophenol side of the diagram. The thaw point – melting point method, however, is not affected by crystallization velocity, so that the latter method appears to be more accurate here. Comparing our results with those of Bogojawlenski, we find that his eutectic temperature (81.5° C.) is in fair agreement with ours, and probably better than ours, since it is higher, and his value for the composition of the eutectic is approximately the average of our two results. Averaging Bogojawlenski's results and our own, we arrive at the following most probable values for eutectic conditions:— composition = 57.8% picric acid, temperature = 80° C.

The System: Trinitrotoluene – Dinitrophenol

The equilibrium diagram of this system is much more satisfactory than that of picric acid – dinitrophenol. This may be due to the fact that a visual check (first appearance of crystals) was made on the thermal analysis. Although the visual method is subjective, it cannot give values that are too high, because crystals must appear before they are seen.

The System: Picric acid–Dinitrophenol – Trinitrotoluene

It was impossible to determine freezing points in this system by thermal analysis. Even the visual method was uncertain because of a natural opalescence of the melt. The composition given by us as that of the ternary eutectic may not be exact, since the thaw point and melting point did not coincide for this or any other mixture. On the other hand, this may only be due to the fact that we deliberately used the materials of the explosive industry, without further purification.

VISCOSITY AND VELOCITY OF CRYSTALLIZATION

Table VII (*a*) shows that picric acid is about 4.5 times as viscous as dinitrophenol, at the same temperature, but the velocity of crystallization is about 10 times as great as that of dinitrophenol for the same degree of supercooling. Hence the velocity of crystallization is highly characteristic, and although decreased by viscosity, the latter is not a determining factor between two different substances.

It has been observed by previous workers, as well as ourselves, that the crystallization velocity of mixtures is irregular, owing to concentration changes, but this difficulty is not met with in the case of eutectic mixtures, since there is no concentration change during crystallization, and constant values for crystallization velocity are therefore obtained.

When picric acid and dinitrophenol are mixed, it might be expected that the crystallization velocity would lie between the values for the pure substances, as with the viscosities, but this is not so. A 60% picric acid mixture, which might be expected to have a crystallization velocity higher than that of pure dinitrophenol, is actually found to possess a crystallization velocity only 1/85: the temperatures are not strictly comparable, but the difference is too great to be accounted for on this basis. The cause of this is perhaps to be found in the tendency of the molecules of dinitrophenol to interfere with the formation of the crystal lattice of picric acid, and conversely.

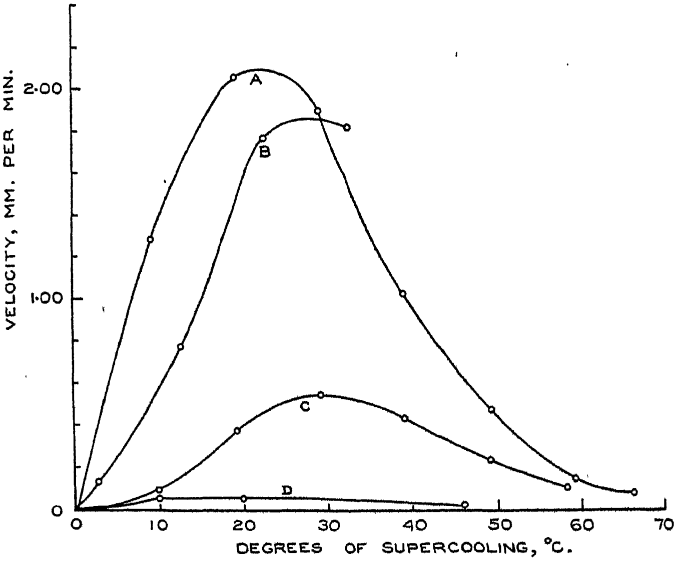

FIG. 3. *Velocity of crystallization of two- and three-component systems.*
A—60% picric acid : 40% dinitrophenol
B—28% dinitrophenol : 72% trinitrotoluene
C—55% picric acid : 45% dinitrophenol
D—Ternary eutectic.

The concentration of the second component, however, does have an effect on crystallization velocity, as would be expected, e.g., a mixture containing 60% picric acid (Shellite) has a maximum crystallization velocity of almost four times that of a 55% mixture. The crystallization velocity seems to depend on whether the mixture lies on one or the other side of the eutectic composition. If, instead of 60% picric acid, a 55% mixture had been used, Shellite would have crystallized much less readily.

By adding 1% guncotton to the 55% picric acid mixture, the viscosity is increased about 8 times, but the crystallization velocity increases about 1.2 times. This is explained by the work of Freundlich and Oppenheimer (4), who showed that non-spherical colloidal particles increased the crystallization velocity. Since the molecule of guncotton is probably long chain, and of colloidal dimensions, the increase is accounted for. Three per cent of guncotton increases the viscosity beyond the measurable limit (30 poises), without reducing the crystallization velocity very much. The effect of increased viscosity at constant temperature is, of course, always to reduce the crystallization velocity.

An examination of Fig. 3 shows that the two component systems have crystallization velocities higher than that of the three component system made from them. This is no doubt due to some extent to the fact that the ternary system, which melts at a lower temperature than any of the component binaries, probably has a higher viscosity than any of the binaries, but this effect is insufficient to account for the very great decrease in crystallization velocity. It seems a general rule that the crystallization velocity of mixtures is lower than those of the components, quite apart from considerations of viscosity.

None of our curves expressing velocity of crystallization as a function of supercooling show a region of constant velocity of crystallization, as in Tammann's experimental work. A maximum value is attained, at 20° to 30° C. of supercooling, which then rapidly decreases.

General Conclusion

The purely practical, war-time problem, viz., that of obtaining an explosive containing picric acid which should remain for a long time in the vitreous state has been only partially solved. We did indeed obtain a mixture, containing picric acid, dinitrophenol, and trinitrotoluene, which would remain in the liquid state at room temperature and crystallize only very slowly, but the melting point of this mixture is too low for a shell filling. Interesting data on crystallization velocity have, however, been incidentally obtained. It will be shown in a subsequent paper that the problem is practically solved by the use of a Shellite containing picramide.

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A PERIODIC ARRANGEMENT OF THE ELEMENTS[1]

By D. F. Stedman[2]

Abstract

A cyclic spiral arrangement of the elements is discussed. This arrangement is best considered as the vertical projection of a solid model, somewhat conical in form. The planar arrangement is modified from the plan of the solid model only as necessary to clarify the presentation.

Considered chemically this arrangement has the advantage of separating each type of element without ambiguity, and the rare earths and 'VIII groups' are also accommodated as an integral and significant part of the orderly development of the table. The *A* and *B* grouping is also eliminated.

The opposing nature of the electropositive and electronegative elements is clearly shown, and the various broad classes of elements are closely grouped, e.g., the active : inactive metals; elements forming predominantly inorganic groupings : elements readily forming organic compounds; the acid forming elements; the various analytical groups, etc.

The table also requires a minimum of artificial arrangement and utilizes a definite scale in both the planar and solid model.

This proposed arrangement of the elements is best considered as a solid model, views of which are shown in Figs. 1 and 2. The planar form is shown in Fig. 3, fundamentally a plan of the solid form, modified only as necessary to produce satisfactory spacing between the elements.

Three Dimensional Model

This model is based on a fundamentally conical arrangement, hydrogen being at the apex and the series of elements being arranged in a spiral, 4 mm. vertical separation being allowed for each element in the actual model shown in the illustrations.

It is intended to be considered that there are three types of spacings between elements; the spacing of elements through the thickness of the model represents the greatest degree of chemical differences, while lesser degrees of difference are represented by the horizontal distances round the surface of the model, these being shown by the thin 'development' lines connecting successive elements. The vertical direction indicates the general families of elements and is shown in heavy lines.

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Contribution from the Division of Chemistry, National Research Laboratories, Ottawa, Canada. Issued as N.R.C. No. 1515.

[2] *Chemist.*

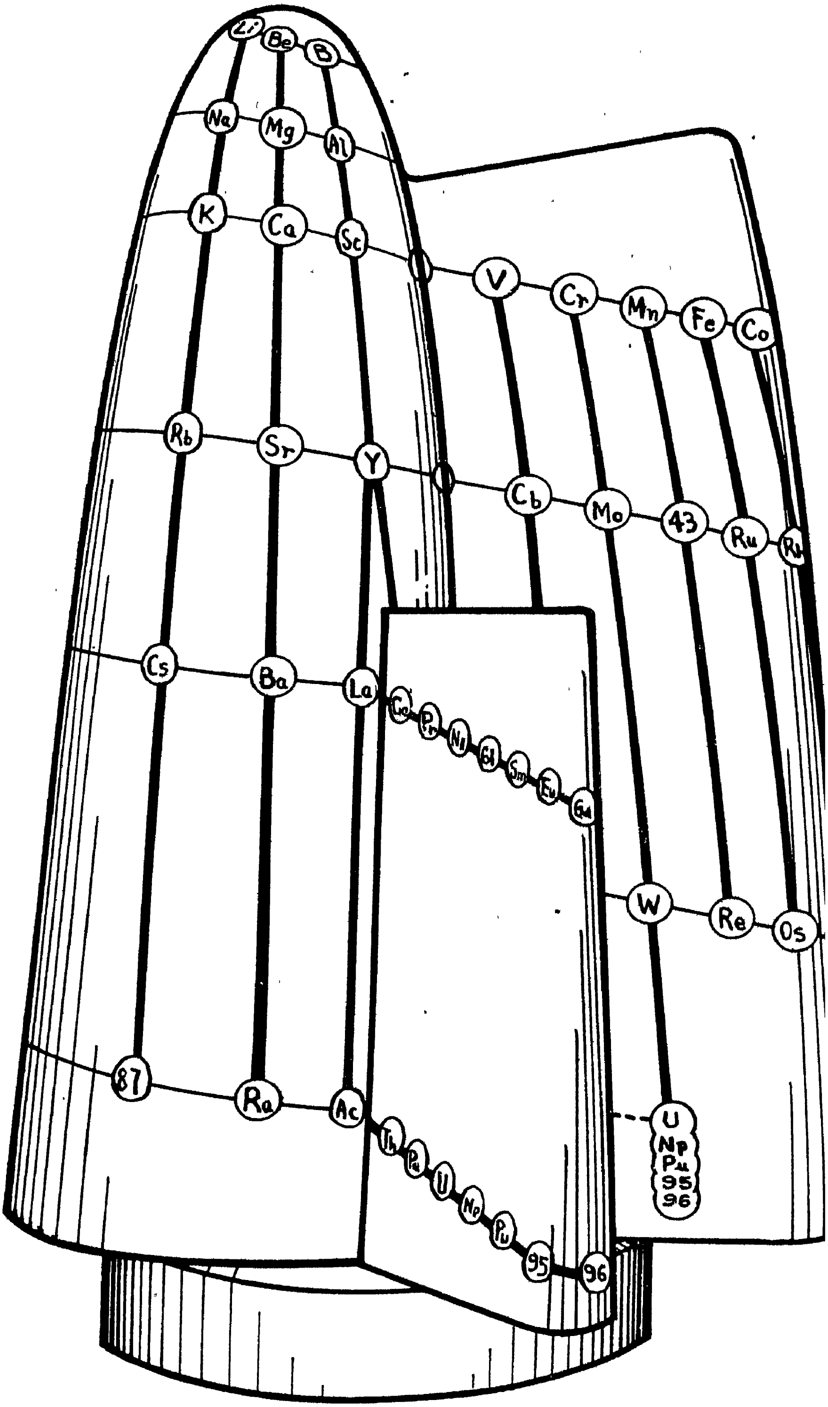

FIG. 1. *Three dimensional model. "Front view". Groups I to VIII.*

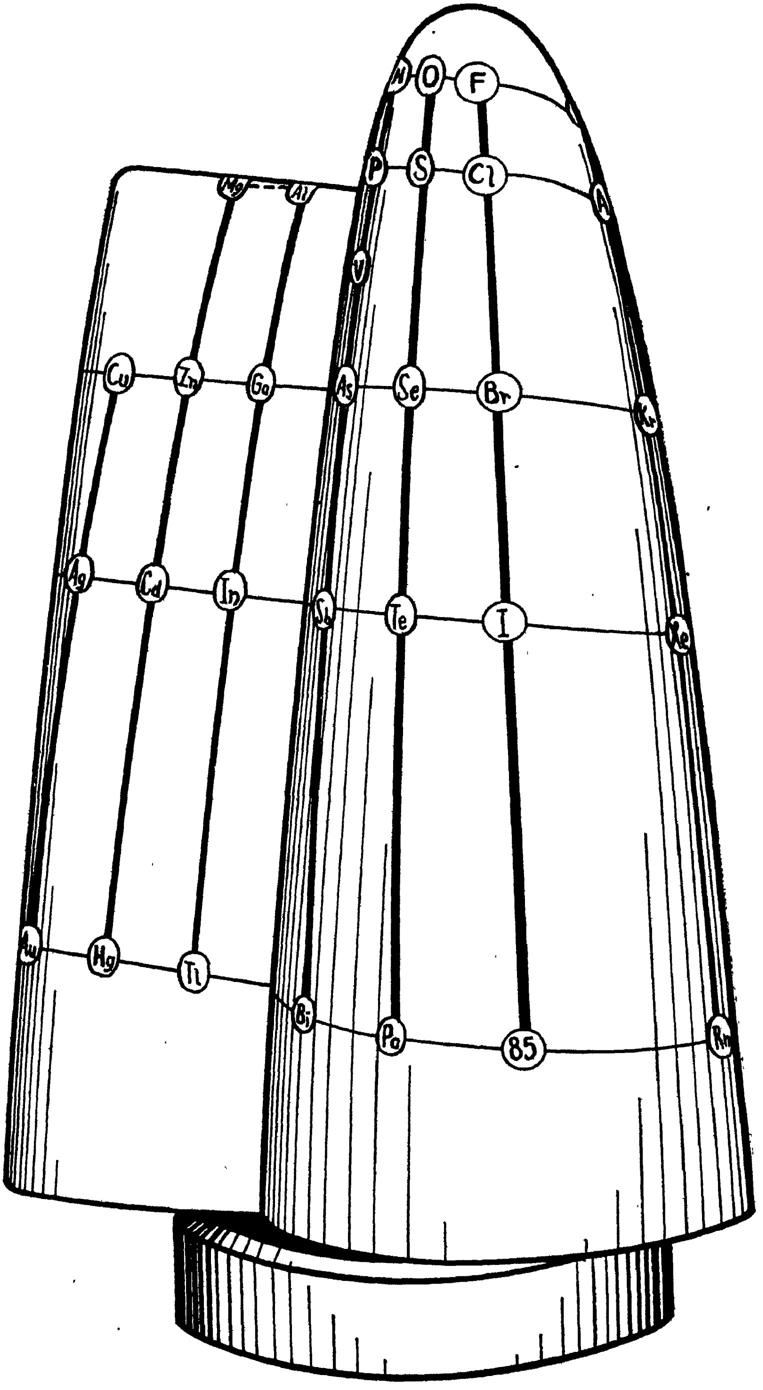

FIG. 2. *Three dimensional model. "Back view". Copper, silver, gold, and electronegative groups.*

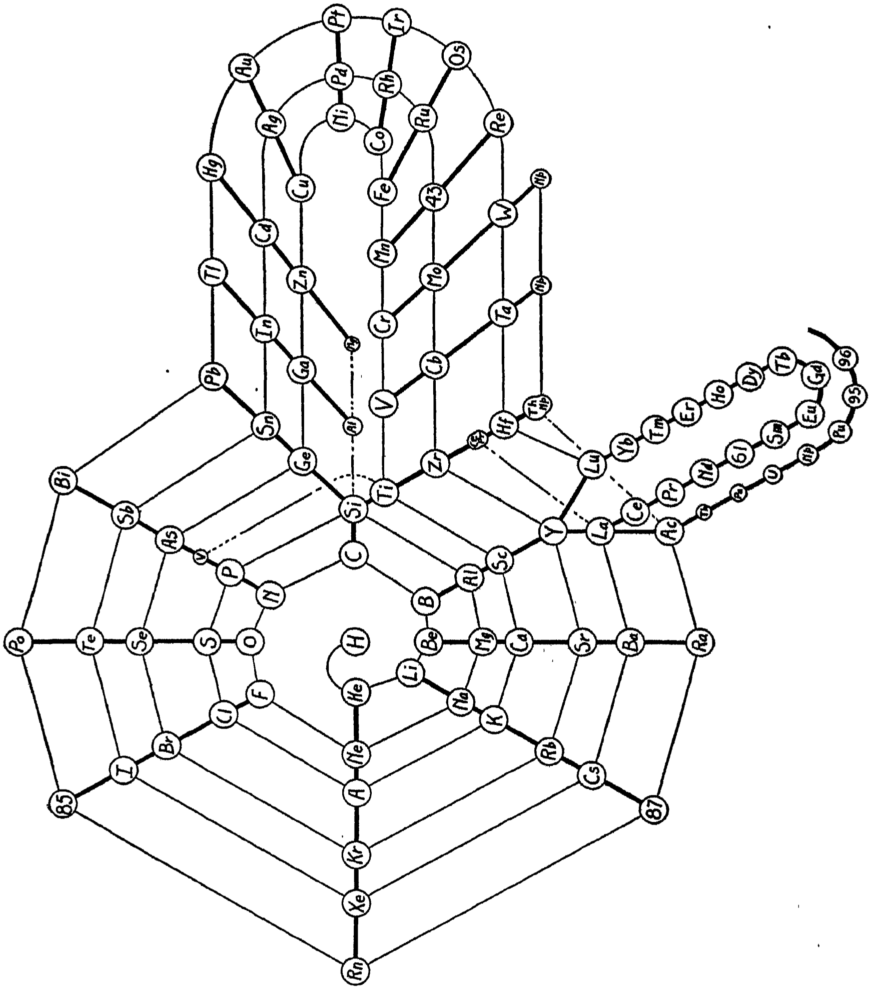

FIG. 3. *Planar diagram.*

It is of course difficult, if not impossible, to maintain a precisely scalar thickness through such a model to indicate all degrees of chemical differences, especially in view of the fact that differences occur not only in degree, but also in type. This model however attempts to indicate the broad classes of variation as nearly as possible by the various directions on or through the model.

The model consists of three parts:—

(*a*) A cubic paraboloid of revolution accommodating the main octet families, typified by all elements up to titanium. This part of the model uses a cubic relation between the thickness and vertical dimension in order to illustrate the great differences between elements on opposite sides of the model by interposing a considerable thickness between them.

(*b*) An 'extension' attached to one side of parabolic section, completed by half of a paraboloid of revolution. The second power relation of thickness to vertical distance and thinner section is used in this part of the model to illustrate that differences although considerable are less than in the main octet groupings, and elements from vanadium to gallium with corresponding families of higher atomic weight are grouped on this section.

(*c*) Another smaller extension, of acute triangular section, is also provided for the rare earth families, the first power relation and very thin section here illustrating the very small differences between opposite elements, and in this region the thin development line is changed to the thick family line for the same reason.

Planar Diagram

This is to be considered as a plan of the solid, but slight changes from direct vertical projection give a more satisfactory presentation. Thus the radial scale from hydrogen in this diagram is proportional to the square root of the atomic number instead of cube root; otherwise the higher atomic numbers are too crowded when reduced to a fairly small diagram. The line from titanium to iron is also drawn parallel to the line from copper to germanium, and similarly with the other development lines in homologous groups. The spacing between these parallel development lines also follows by projection from the initial and final elements, titanium, germanium, etc., as the case may be, rather than by vertical projection from the solid. These scalar changes, or the scales themselves, are of course merely aids in drawing, and are not of actual significance in the arrangement. Apart from such minor changes both diagrams are interchangeable and will be considered together, as the organization and groupings are identical in both.

The planar arrangement is superficially similar to several other spiral arrangements, e.g. that proposed by K.G. Irwin (1), but so far as the author is aware none of these other classifications assist much in illustrating or clarifying the *relations* between the elements, on which the present arrangement is based.

General Groupings in the Arrangement

Main Cubic Paraboloid 'Cone'

It will be seen that this portion of the arrangement follows the types of the first two and a half 'short periods', the eight elements of each cycle being arranged in the planar form as a spiral of radius increasing as the square root of the atomic number, while in the model each successive element is 4 mm. lower than the preceding. The angular distribution of the families is arranged as nearly as may be to illustrate the degree of difference between each family, the greatest spacings being provided in both directions from the zero group.

One of the major features of this arrangement is that only two families are considered as true branched families, instead of seven as in the Mendelejeff system, and of these two, one, at yttrium, is not usually considered in this manner.

Consider the branch at silicon first. The family carbon, silicon, germanium, tin, lead is an excellent and continuous family, especially in relation to their organic compounds, while carbon, silicon, titanium, zirconium, hafnium is almost as closely a related family, especially in relation to their inorganic compounds. In general all elements on the germanium side of the table give organic compounds very readily, while, after crossing the mid-line of the diagram, this property rapidly diminishes.

On considering the process of building up the heavier elements, starting at hydrogen, the first two short periods are quite homologous, but after passing titanium, the next element, vanadium, shows many properties quite different from those of phosphorus, and this is indicated by the branch in the development line, by placing vanadium on the side extension. However, vanadium also shows some properties very much like those of phosphorus, and consequently vanadium is also shown in the phosphorus family, as a smaller circle, indicating that only a part of the properties of vanadium are represented by this small circle. The development line leading to this partial of vanadium is shown dotted.

In this arrangement vanadium is therefore called a transition element, and in this discussion the usual use of this term, e.g., as frequently applied generally to rare earths and often VIII group elements, etc., is abandoned, since these elements have here an orderly and significant position.

Transition elements here considered are therefore those elements which occur immediately following a change in development, and which act partially as if such a change had not occurred.

It might also be noted that the use of small symbols to illustrate the partial nature of such transition elements as vanadium in the phosphorus family is not of course necessary, but is merely offered for consideration.

This transition effect may also be considered as continuing to a very slight extent with both chromium and manganese, but in these cases the similarity to the sulphur and chlorine families respectively is restricted to one class of compound in each case, the chromates and manganates being similar to the sulphates, and the permanganates being similar to the perchlorates. It seems hardly necessary to indicate such abbreviated similarity in any definite manner in the table.

In further consideration of transition effects at this branch, it is clear in the next turn of the spiral that columbium does not show any perceptible resemblance to arsenic and consequently transition effects are restricted mainly to vanadium at this branch from the main octet families.

Main Side Extension

Elements following vanadium are arranged in loops around this side extension, and rejoin the main octet again on reaching germanium. The iron–cobalt–nickel triad and the heavier homologues are frequently considered as differing from their neighbours, and consequently in many tables all nine elements are grouped together as Group VIII. In the present arrangement it is considered that the whole process from vanadium to nickel is continuous, but that the chemical difference for each step becomes successively less. In order to show this the spacings along this development line decrease continuously from vanadium to nickel.

Following nickel, however, chemical differences again become quite marked, and elements are therefore evenly spaced again from nickel to germanium, the same arrangement being followed for each of the homologous triads.

It might perhaps be noted that although, for instance, manganese and zinc are not very far apart, particularly in the planar form, it is not intended to suggest that they are actually chemically similar. These groups of elements are on opposite sides of the solid model and the thinness of this section is merely intended to express the fact that the difference between elements on opposite sides is here much less than for those on opposite sides of the main octet series.

The development lines in passing round this side extension rejoin the main octet series at germanium, tin, or lead, as the case may be. The major criterion is of course that these elements are again able to complete an inert gas shell by adding electrons equal in number to their maximum valence, and they are therefore again in this respect similar to carbon and silicon. The elements on the titanium to thorium branch, however, cannot complete such a shell by adding any available number of electrons, and in this respect they differ from silicon and therefore represent the start of a change in the development of immediately following elements.

Rare Earth Extension

The above discussed branch in the silicon families, to titanium and germanium respectively, results from the continued addition of peripheral electrons, causing what might be termed overloading and structural weakness in the underlying electronic foundations in the atom. Thus the inner electronic structure is then unable to support more peripheral charge and the addition of further electrons necessarily results in 'stiffening' the inner electronic structure before the external electronic loading can be increased. However, in the case of the silicon branches the level considered is only one level below the valence electrons, and is still open to chemical attack. Hence the added electrons produce considerable chemical difference for each added electron. Although this is of course all well known, the usual periodic tables do not indicate these processes as clearly as the present arrangement or the abrupt start of these processes at vanadium.

The electronic processes concerned in the structure of the rare earths are quite analogous to the electronic effects resulting in the production of the two silicon families, but in the case of the rare earths the inner electronic weakness is more deep-seated, the added electrons reaching two quantum groups further in the atom. The chemical differences therefore are of course very slight, and in the usual periodic table the rare earths are placed in an appendix of some sort, as peculiar to themselves.

However, this procedure is unnecessary in the present arrangement and the yttrium branch is developed exactly as the silicon branch, which it resembles in many ways, even in detail. Thus silicon shows greater resemblance to germanium than it does to the closer titanium, while yttrium similarly shows greater resemblance to lutecium than to lanthanum.

In this rare earth group it will be seen that immediately following the change in development at lanthanum, cerium and praseodymium show transition effects exactly analogous to the effects noted with vanadium, and appear also as IV state in the zirconium family.

The next cycle of elements starting from actinium, of still heavier elements round the rare earth loop, are not usually considered as rare earth members and although the author drew this table in this manner 16 years ago (up to uranium of course) the evidence was then rather scanty. Until recently the major evidence suggesting this arrangement was:—

1. Primary rare earth minerals are never found without either thorium or uranium.

2. Primary thorium and uranium minerals are never found without rare earths.

3. Uranium is not associated with tungsten in minerals.

4. Although thorium shows exclusive tetravalence, this does not necessarily suggest that the rare earth development is abandoned in the actinium cycle. The tetravalence of thorium in fact might be expected to be strongly developed, as cerium shows definite transition to IV state, and the larger ionic diameter of thorium and its more metallic nature would suggest that this transition would in any case be much more marked than with cerium. It might be noted in passing that the effects discussed in comparing thorium with cerium are exactly the opposite of those noted in comparing columbium with vanadium, as related to transition effects. In the next heavier cycle following vanadium the *more* metallic nature of columbium greatly *reduces* the probability of transition effects and in fact with columbium no transition is detected,

although columbium with respect to the silicon families is in a position quite comparable with that of thorium with respect to the yttrium families.

5. The fusion point of uranium element is much too low for any close relation with tungsten and all its neighbours.

6. Chromium, molybdenum, and tungsten are also fairly easily reduced and also increasingly inert, while uranium differs very greatly in both properties.

7. Furthermore, tungsten is not a good 'carrier' for uranium, i.e., they are rather easily separated in many reactions.

8. The absorption spectrum of uranium compounds is strongly suggestive of the rare earth type.

These properties taken together rather strongly suggest that uranium is partially reverting to an eka-rare-earth cycle, and on this basis it was so arranged.

The present work on elements heavier than uranium, although not yet reported very fully, certainly confirms this arrangement of the elements (2), since plutonium is reported to reach VI state only with definite oxidation, while 95 and 96 become increasingly stable in III state and show chemical properties increasingly similar to those of the more familiar lanthanum family. This gradual change in the actinium family from transition to rare earth types is quite analogous to the effects in the lanthanum family, but being so much more extensive in this arrangement it is indicated by the gradual increase in size of the symbols; this again however is of course not a necessary factor.

In the tabular arrangement neptunium is included as the typical fully developed transition element, since it is reported to give all states from III to VI with fairly uniform ease. Although the chemistry of neptunium is not widely known at present, this will doubtless be corrected.

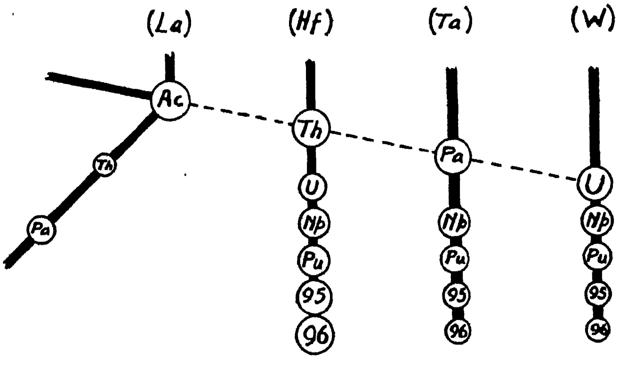

FIG. 4. *The actinium group transition elements.*

In the table, owing to the closeness of elements differing by one unit in atomic number, grouped with thorium in the transition states IV to VI, it is not possible to show all these transitional elements without distortion of the scale. This portion is given fully on the model and is therefore enlarged in Fig. 4.

It might be noted that for convenience in using the model, this extension for the rare earth loops is readily removable, being held in place by two small wooden pins.

General Discussion

It will be seen that all the usual groups of elements are well organized, and, including the transition elements, are clearly separated without overlapping. The usual analytical groups are also closely organized; thus the insoluble chlorides include those of polonium, bismuth, lead, thallium, mercury, copper, and silver. The sulphides insoluble in acids are enclosed roughly in the line through selenium, germanium and cobalt, while sulphides insoluble in ammonia pass still further down the table, and it will be seen that these groupings cross the broad divisions of the table, without suggesting that these divisions are artificial.

Other Transitional Effects

A further feature of this arrangement is that all transitional effects can be clearly indicated and their origin understood. These transitional effects are in reality the basis of the usual tabular classifications in which *A* and *B* columns of elements are placed together, but in the usual columnar table the origin and limits of these effects are not clear.

The transitional effects noted with vanadium have already been discussed in some detail, and the effect shown to exist as far as manganese along the development line. Although transition effects with chromium and manganese are limited to chromates, manganates, and permanganates, within these classes the transition effect is very strong, as similarity to the sulphur and chlorine analogues is very close. This transition however does not extend to the next heavier family, columbium and molybdenum.

The cerium–praseodymium transition has also been discussed and the effects noted in the actinium family. In this latter family the transition region might be considered as greater than any transition shown elsewhere in the table, but it should be noted that the vanadium-manganese transition bridges the range from group IV to group VII elements, or covers the same range as that shown by the actinium family from groups III to VI. This latter group is peculiar in that so many elements show this effect, but when it is noted that this is a rare earth group, where elements are not expected to differ greatly, and also that the increased ionic radii greatly stimulate polyvalence, the effects noted do not appear greater than those that should be expected.

A further type of transition is however noted following nickel, palladium, and platinum. These elements are at the turning point of the loops, and are the end members of an inner electron process. This process reaches its limit at nickel, palladium, and platinum, and these elements show a remarkable inertness (in which property platinum shows the greatest development), differing only in degree from that of the entirely inert zero group. This group therefore functions as another starting point for the additon of peripheral valence electrons in a somewhat similar manner to the development of the active metals. The chemistry of the elements produced by this process, starting with the copper family, is however greatly different and much more complex than the effects noted in the sodium family with its single valence electron and absolutely inert core.

It will be seen therefore that the development of the 'front' of the table from lithium on the left resembles somewhat the development of the 'back' of the table from copper on the right, and as more valence electrons are added in each case the similarity becomes more marked.' Thus when four electrons are added to both series the resulting elements are so similar that they are classed as the main silicon branched families. When still more valence electrons are added, the differences become more marked again but, for the elements grouped round sulphur and those grouped round molybdenum, their acid forming properties in both cases are major features of their chemistry. Thus the 'front' and 'back' of the table develop throughout with much similarity, and it is felt that this arrangement illustrates this effect much more clearly than previous methods.

Transition Effects with Copper, Silver, and Gold

When nickel–palladium–platinum are considered in detail it is clear that the greater stability of the palladium core confers almost definite monovalence on silver, although a few divalent silver compounds are known. With copper and gold however the lesser stability of the nickel and platinum cores still permits the ready removal of electrons from these inner levels, and confers higher valence on copper and gold.

Thus copper II, gold III, and silver II in the few cases known to occur, may properly be considered as transition effects of exactly the same class as that defined earlier, as these polyvalent effects relate solely to the change in development occurring at the nickel family considered as a pseudo-zero group.

Reversed Transition

A still different type of transition is also to be considered. Since Nature can hardly recognize 'up' or 'down', or the development of elements from either light or heavy atoms with any special distinction, transition effects as here defined, if valid, should occur with the same definition, i.e., immediately following changes in the development pattern, but considered as starting from the heaviest atoms.

In starting from the heaviest elements and passing clockwise round the table, the first cycles establish the 'normal' pattern for this direction as passing round both extensions, and the first deviation from this pattern occurs at yttrium. The next element, strontium, therefore must be examined for transition effects. Since strontium however has only two electrons external to its absolutely inert core it cannot remain trivalent and assume transitional properties in a manner analogous to the development of ytterbium from lutecium, since this requires trivalence, a condition absolutely impossible with strontium, as only simple ionic compounds need be considered in this part of the table.

On continuing the development pattern, passing round only the main extension, the next change occurs at silicon, and aluminium must therefore be examined in the same manner. It will be seen on the table that aluminium and magnesium are given places in the gallium and zinc families, respectively, since these two elements do show strong transitional effects referring to these positions. In many ways the properties of aluminium and magnesium strongly resemble those of the gallium and zinc families, and in these properties aluminium and magnesium do not resemble the earth families. Thus the respective portions of the properties of aluminium and magnesium are divided accordingly, in the same manner as is done with those of the other transition elements.

Comparison with Mendelejeff Table

It will be seen that the stronger transitional effects here discussed, i.e., those noted for vanadium, cerium, thorium, aluminium, magnesium, and the branched silicon family are the basis for the usual columnar arrangement of the elements into *A* and *B* groups. Thus the real resemblance between these groups is limited to these transition effects, and when these properties are separated in the manner described, the need to consider the *A* and *B* elements in a forced similarity is no longer required It is therefore felt that the present arrangement gives so much more insight into the orderly development and classification of the elements that its somewhat greater complexity is merely a reflection of the actual complexity of chemistry itself. When these complexities are properly separated and grouped their orderly consideration and study are greatly simplified.

Acknowledgments

Grateful acknowledgment is made of useful discussions regarding this arrangement of the elements with Col. E. A. Flood, Department of National Defence; and also of assistance in drafting and constructing the model by Mr. P. Langevin, Mrs. S. Sterns, and Mr. M. Couture.

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THE EQUILIBRIUM DATA AND CRYSTALLIZATION CHARACTERISTICS OF THE SYSTEM: PICRIC ACID - DINITROPHENOL - PICRAMIDE[1]

By A. N. Campbell,[2] E. J. Pritchard,[3] A. J. R. Campbell,[4]
and M. L. Boyd[3]

Abstract

The equilibrium data of the systems: picramide - 2,4-dinitrophenol and picric acid - picramide, have been obtained. The ternary eutectic of the system picric acid - picramide - dinitrophenol has also been obtained. Because of the low crystallization velocity of picramide, it appears that the problem of finding a picric acid mixture of the nature of Shellite, i.e., one containing picric acid and dinitrophenol, which should crystallize only slowly at room temperature, so that the cavity produced by contraction should be accessible to refilling and not cause cavitation, is solved by the use of a Shellite mixture of the following composition: 53.0% picric acid, 41.0% dinitrophenol, 6.0% picramide; this mixture melts at 77° C.

The essence of the problem here investigated has been stated in a previous paper (1), viz., the production of a Shellite that would not crystallize, or only slowly crystallize, at room temperature. The work of the previous paper shows little or no approach to a successful solution. In the present paper, a mixture that crystallizes very slowly is described and to this extent the problem is solved. Even so, however, special precautions would have to be taken to ensure that crystallization proceeded in the desired manner, i.e., from the outside of the shell inwards.

Picramide is known to be a substance of very low crystallization velocity. We therefore added picramide to Shellite with the object of so reducing the crystallization velocity that the Shellite might be induced to become vitreous. Presumably, the explosive power would not be much, if at all, reduced, since picramide is itself an explosive. Too much picramide could not be added, lest the melting point were reduced below the service limit.

The component binary systems of the ternary system: picric acid - dinitrophenol - picramide are picric acid - dinitrophenol, picric acid - picramide and picramide - dinitrophenol. Of these, the two former have already been investigated. The system: picric acid - dinitrophenol is the Shellite system, dealt with in our previous paper (1). According to International Critical Tables, the system picric acid - picramide has a eutectic melting at 113.5° C. and containing 25 mole % picramide: the original reference was not available (2). It remained to investigate the binary system: picramide - dinitrophenol.

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[1] *Manuscript received November 5, 1946.*
Contribution from the Department of Chemistry, University of Manitoba, Winnipeg, Man.

[2] *Professor of Chemistry and Head of the Department.*

[3] *Holder of a Bursary under the National Research Council of Canada, 1942-1943.*

[4] *Wife of the senior author.*

Our investigation of the ternary system, however, led us to doubt the accuracy of the data given for the picric acid – picramide system, and we therefore investigated this system ourselves; there is no doubt the published data are incorrect.

Experimental

Equilibrium Data

The picramide was supplied by Dr. G. Wright of Toronto University. It had a melting point of 185.5° to 186.5° C. (value given in the literature = 188° to 190° C. (Beilstein)). The preparation was recrystallized from glacial acetic acid, after which it had a melting point of 185.5° to 186.5° C., i.e., the recrystallization had not affected the purity. This recrystallized product was used in the work described below.

The system: picramide – dinitrophenol was first investigated by thermal analysis, with very indefinite results, owing to the low rate of recrystallization of the melts. The results are given in Table I.

TABLE I

Wt. % picramide	Freezing temperature, ° C.	Eutectic temperature, ° C.
0.0 (100 % dinitrophenol)	110.9	—
10	106	None observed
20	100.8	100.0
30	103.9	100.3
40	128.3	100.4
50	146.8	100.6

The system was then investigated by means of the thaw point – melting point method, with much better results. These results are given in Table II.

TABLE II

Wt. % picramide	Thaw point, ° C.	Melting temperature, ° C.
10	100.5	106.2
20	98	101.5
25	99	104.5
30	100.5	113.3
40	100.0	129.5
50	—	143.0
60	—	153.0
70	—	163.0
80	—	173.0
90	102.0	180.5

When the melting point results are plotted, two curves intersecting at 22.5% picramide and a temperature of 100.2° C. are obtained. The eutectic composition was checked by direct experiment: a mixture containing 22.5% picramide had a thaw point of 99.5° C. and a melting point of 101° C.

Density of Liquid Eutectic Mixture

This was determined at 110° C., as $d_4^{110°} = 1.478$. Taking the densities of solid picramide and solid dinitrophenol as 1.762 and 1.683, respectively, the contraction on filling a shell at 110° C., crystallizing, and cooling to room temperature, is roughly 13% of the total volume; this is higher than the contraction of ordinary Shellite.

Viscosity of Liquid Eutectic

TABLE III

Temperature, ° C.	Viscosity, centipoises	Temperature, ° C.	Viscosity, centipoises
110	5.96	95	8.44
106	6.39	91	11.16
100	7.53		

The Ternary Eutectic: Picric Acid – Picramide – Dinitrophenol

The approximate composition of this eutectic was obtained by joining the compositions of the binary eutectics to the opposite angular points of the triangular diagram. The small triangle formed by the intersection of these three straight lines may give an approximation to the ternary eutectic composition, depending on how straight are the binary eutectic troughs. Mixtures in this neighbourhood were prepared and examined by the thaw point – melting point method. The results are contained in Table IV.

TABLE IV

THE TERNARY EUTECTIC: PICRIC ACID – PICRAMIDE – DINITROPHENOL

Point No.	Composition, %			Thaw point, ° C.	Melting point, ° C.
	Picric acid	Picramide	Dinitrophenol		
1	50.0	11.5	38.5	74.0	86.5
2	47.0	16.0	37.0	74.0	98.0
3	41.0	13.5	45.5	—	90.5
4	53.5	5.0	41.5	74.0	77.5
5	53.0	6.0	41.0	74.0	77.0
6	52.0	8.0	40.0	73.5	78.5
7	52.5	7.0	40.5	73.4	79.0
8	52.0	6.0	42.0	73.5	77.1
9	52.0	5.0	43.0	73.5	78.5
10	54.0	6.0	40.0	—	78.3

Point No. 5 has the lowest melting point and therefore the composition of the ternary eutectic cannot be far from 53.0% picric acid, 41.0% dinitrophenol, 6.0% picramide, melting at 77.0° C. Point No. 8 fulfils the eutectic condition almost equally well.

The System: Picric Acid – Picramide

Since the triangle formed by the intersection of the lines drawn from the pure components to the opposite binary eutectic, on the triangular diagram, was displaced considerably from the ternary eutectic composition given above, it seemed to us that the data of the system picric acid – picramide, as given in the International Tables (2) were incorrect. These data are:— eutectic temperature, 113.5° C.; eutectic composition, 25 mole % picramide = 25% picramide by weight. We therefore repeated this system by the thaw point – melting point method, with the results as given in Table V.

TABLE V

EQUILIBRIUM DATA FOR THE SYSTEM: PICRIC ACID – PICRAMIDE

Weight % picramide	Thaw point, ° C.	Melting point, ° C.
10	—	117.0
14	—	115.0
15	112.5–113	114.0
16	112.5–113	114.5
20	113.0	121.0
25	113.0	124.5
40	—	146.0
70	—	168.5

The above data, when plotted, indicate a eutectic composition of 15.5% picramide, melting about 113° C.

Crystallization Characteristics of the Ternary Eutectic

No quantitative measurements were undertaken, as the exigencies of war work called our attention to other things, but the following qualitative observations were made. A large test-tube was filled with the ternary eutectic. Shrinkage took place on cooling, but the melt did not shrink away from the sides of the tube, but from the centre of the free surface. The hollow thus formed could have been filled with more molten explosive. The density of the liquid ternary eutectic was determined at 78.2° C. as $d_4^{78.2} = 1.56$. From this, the contraction on filling (without refilling) results as 9.76% as compared with 10.78% for the binary mixture 55% picric acid – 45% dinitrophenol, and 10.99% for 60% picric acid – 40% dinitrophenol (ordinary Shellite).

Conclusion

The problem of finding a picric acid mixture of the nature of Shellite, i.e., one containing picric acid and 2,4-dinitrophenol which should crystallize only slowly at room temperature, so that the contraction produced should be accessible to refilling and not cause cavitation, is solved, in our opinion, by the use of a Shellite mixture of the following composition: 53.0% picric acid, 41.0% 2,4-dinitrophenol, 6.0% picramide: this mixture melts at 77° C.

References

1. Campbell, A. N. and Pritchard, E. J. Can. J. Research, B, 25 : 183-197. 1947.
2. Efremov, N. N. J. Russ. Phys. Chem. Soc. 50 (I) : 441-459. 1918.

A STUDY OF SYSTEMS INVOLVING TRINITROTOLUENE, RDX, NENO, AND DINITROBENZENE, WITH PARTICULAR REFERENCE TO THE COMPOSITION OF THE BINARY EUTECTICS[1]

By A. N. Campbell[2] and H. A. Kushnarov[3]

Abstract

The eutectic temperature and composition were determined by thermal analysis for the systems: TNT–RDX, TNT–NENO, and DNB–NENO. The velocity of crystallization of pure RDX, as well as of the eutectic mixture of TNT–RDX, was studied. Density determinations were made on the pure materials, TNT, RDX, NENO, and DNB, as well as on the eutectic mixtures mentioned above. Where possible, the densities of both molten and solid forms were determined, and the contraction on solidification calculated. An attempt was made to establish the existence of a transition point in the allotropic transformations of NENO. The attempt failed, possibly because the allotropy is monotropic: there seems no reason to doubt the existence of allotropic modifications of NENO.

Introduction

The most satisfactory method of shell filling consists in pouring the molten explosive into the shell and allowing it to solidify slowly. This requires that the material in question should have a melting point that is easily accessible under factory conditions, that is, below the temperature of saturated steam. In this respect trinitrotoluene has proved to be ideal, since its melting point is 80.8° C. When, however, an explosive is mixed with another substance, the melting points of both are lowered, in the absence of solid solution or complete immiscibility in the liquid state. In a simple binary system, the eutectic mixture has the lowest melting point and therefore a knowledge of the eutectic temperature and composition in any binary explosive system is of the highest importance in this connection. Since RDX and NENO are too sensitive to be used unmixed, the eutectic conditions of their admixture with TNT become of interest.

Not only is an upper limit of melting point imposed by factory conditions, but conditions of service impose a lower limit. This lower limit is considered to be about 60° C., since, under tropical or accidental conditions, the temperature of a filled shell might approach this. If incipient, that is, eutectic, melting were to take place below this temperature, the efficiency might be reduced or destroyed, or it might even become a danger to the user. Thus, mixtures used for shell filling should have eutectics lying between 60° and 100° C.

It is well known that most liquids contract on solidification. If a molten explosive cools within a shell, the contraction resulting upon solidification may lead to serious cavitation. If the cavity occurs under the booster, the

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Contribution from the Department of Chemistry, University of Manitoba, Winnipeg, Man.
[2] *Professor of Chemistry and Head of the Department.*
[3] *Holder of a Bursary under the National Research Council of Canada, 1943-1944.*

shell may fail to explode, or the shock of the set-back across a cavity in the rear of the charge may cause the shell to explode prematurely. If the contraction occurs at the top of the charge, the cusp formed may be filled up with more liquid explosive, but if cavities occur throughout the body of the cast, this is not possible. The former state of affairs is more likely to be produced if crystallization occurs slowly, and this can be brought about by adding to the melt a substance that reduces velocity of crystallization.

An ideal explosive, from the point of view of cavitation, would be one in which the density of the melt is identical with that of the solid form. Such a substance would show no contraction on solidifying and the problem of cavitation would be almost entirely eliminated. The new explosive NENO appears to approach this requirement, since, it is said, the density of supercooled liquid NENO at 30° C. is 1.63 gm. per cc., while the density of the solid, at the same temperature, is 1.67 gm. per cc., giving a contraction on solidification of only 3.4%. NENO may be cooled to room temperature without crystallization taking place, that is, it enters the vitreous state. Trinitrotoluene, on the other hand, undergoes spontaneous crystallization before it can be cooled to a point where it might be expected to form a glass.

The first aim of the present work was to discover whether mixtures of TNT with RDX and with NENO and of *m*-dinitrobenzene with NENO possessed melting points suitable for shell filling by pouring and to find the eutectic compositions, since a suitable mixture would have, in general, a composition not differing greatly from that of the eutectic. The second aim was to reduce the contraction on solidification of any or all of the above mixtures, by reducing the velocity of crystallization and, if possible, causing them to enter the vitreous state.

Experimental

Materials

Trinitrotoluene.—The TNT used in this work was a commercial explosive, which was not further purified, since our interest lay in the behaviour of the factory produced materials, rather than in pure substances.

RDX.—Pure RDX is said to melt at 202° C., and, on this basis, the material with which we were supplied was markedly impure, since it melted at 195.0° C. After the material had been recrystallized from hot acetone and dried over sulphuric acid, the melting point rose to 198.5° C. Further recrystallizations raised the melting point to 199.5° C., but no higher.

NENO.—The melting point of NENO has been variously stated to lie between 88.5° and 91° C. It appears, however, that earlier preparations were impure and that the true melting point lies between 90° and 91° C. Our material melted at 90.6° C. and therefore was presumably very pure. NENO is reported to be stable up to 105° C. but above that temperature substantial quantities of gas are evolved. Even at 95° C., however, decomposition sets in if the temperature is maintained long enough, say 30 min. NENO is said to exist in two crystalline modifications, an α-form consisting of needles, and a β-form of twinned rhombs. Since a transition temperature of 38° C. is reported, the dimorphism must be enantiotropic. Such allotropic changes in explosive material may be very undesirable, for example, the 32° C. transition of ammonium nitrate is a well known source of trouble. This effect is due to a difference in density of the two modifications and consequent change in volume, which tends to cause a disruption of the charge. It has been shown, however, that while α-NENO has a density of 1.71 that of β-NENO is 1.69; the change in volume accompanying the allotropic change is therefore slight.

**m-Dinitrobenzene.*—Pure *m*-dinitrobenzene melts at 89.9° C.; our commercial product melted originally at 85° to 87° C., but after two recrystallizations from hot alcohol the melting point rose to 89.6° C.

Apparatus

All thermometers were calibrated against standards. The thaw point – melting point apparatus used in this work has been described elsewhere (2). It is therefore unnecessary to describe it here, but the advantage of the method for at least a preliminary survey of systems of which the components are either rare or explosive may once again be stressed.

The apparatus for determining velocity of crystallization has also been previously described (2).

Thermal analysis was carried out in a small tubular electric furnace, using Plato's method of graduated cooling (5).

A special apparatus was devised to determine the amount of 'sweating' of a given mixture at a given temperature, i.e., the amount of liquid exuding from the cartridge. It consisted of a long glass cylinder, about 2 in. in diameter, placed vertically in a thermostat. A 20 gm. cartridge of the desired composition was then cast in a mould, and, as the liquid was solidifying, the end of a wire was inserted in it. A weighed crucible was placed at the bottom of the cylinder and the cartridge suspended immediately above it so that it hung freely without touching the sides of the cylinder. The open end of the cylinder was corked and a thermometer inserted in the cork so that the bulb was immediately above the suspended cartridge. The crucible was removed and weighed at regular intervals so that the fraction of the cartridge that had melted out could be determined.

Other procedures, such as the use of the dilatometer and of a microscope with heated substage, are too well known to require description.

Results

The equilibrium data, obtained by the thaw point – melting point method, for the system TNT–RDX are contained in Table I (*a*), while the same data for the same system by the method of thermal analysis are contained in Table I (*b*). Table II gives the results of calculating the course of the freezing curve for the very dilute range, from the van't Hoff formula, $\triangle T = mK_f$. Tables III (*a*) and III (*b*) reproduce the equilibrium data, by the method of thaw point – melting point and by the method of thermal analysis, for the system TNT–NENO. Table IV contains similar data by the thaw point – melting point method only, for the system NENO–DNB. Measurements of velocity of crystallization are given in Tables V (*a*), V (*b*), and V (*c*). The 'sweating' data, i.e., the percentage amounts melted from a cartridge of given composition at a given temperature in a given time, are reproduced in Table VI (*a*), (*b*), (*c*), (*d*) (*e*). Various density determinations are contained in Table

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**NOTE.—Throughout the paper the abbreviation DNB is used for m-dinitrobenzene.*

TABLE I (*a*)

THE EQUILIBRIUM DATA OF THE SYSTEM TNT–RDX BY THE THAW POINT – MELTING POINT METHOD

Composition, wt. % of RDX	Thaw point, ° C.	Melting point, ° C.
0	76.5	80.2
2	74.8	79.2
4	74.6	79.0
5	75.0	78.7
6	75.1	92.3
7	74.9	103.5
8	75.3	110.8
9	75.0	114.3
10	74.9	117.0
12	74.7	122.0
14	—	126.2
15	74.9	131.5
18	75.5	135.5
20	75.2	140.0
25	74.9	145.8
30	75.0	155.5
35	75.1	159.5
40	74.9	163.5
50	75.0	172.0
60	75.1	177.5
70	74.8	183.0
80	*	*
90	*	*
100	—	198.5

* *Considerable decomposition made these determinations unreliable.*

TABLE I (*b*)

THE EUTECTIC TEMPERATURE OF THE SYSTEM TNT–RDX BY PLATO'S METHOD OF THERMAL ANALYSIS

Composition, wt. % RDX	Eutectic temp., ° C.	Composition, wt. % RDX	Eutectic temp., ° C.
10	78.4	30	78.0
15	77.9	40	77.8
20	78.1		

TABLE II

MELTING POINTS OF TNT CONTAINING SMALL QUANTITIES OF RDX

K = 111.7° C. per 100 gm. TNT

% RDX	Δ T, calc.	Melting point, ° C. (calc.)	Melting point, ° C. (obs.)	Mol. wt. of RDX
2	1.1	79.1	79.2	228
3	1.7	78.5	—	—
4	2.3	77.9	79.0	389
5	2.9	77.3	78.7	390

TABLE III (*a*)

THE EQUILIBRIUM DATA OF THE SYSTEM TNT–NENO BY THE THAW POINT – MELTING POINT METHOD

Composition		Thaw point, ° C.	Melting point, ° C. (expt.)	Melting point, ° C. (calc.)[1]
Wt. % of NENO	Mol. % of NENO			
0	0	78.7	80.4	—
5	3.2	64.6	78.9	78.8
10	6.6	58.2	77.3	77.0
15	10.1	56.6	75.7	75.3
20	13.7	55.4	74.3	73.4
30	21.4	55.6	70.1	68.9
40	29.7	55.2	66.8	63.9
50	38.9	55.6	62.0	57.8
52	40.9	55.3	60.6	—
54	42.9	55.1	62.1	—
60	48.8	55.1	66.2	65.8
70	59.7	55.5	71.9	72.4
80	71.7	55.2	78.2	78.6
90	85.2	55.8	84.7	84.8
95	92.4	60.2	87.8	87.7
100	100	89.7	90.6	—

[1] *The theoretical values for the melting points of the various mixtures were calculated by means of the Washburn and Read equation (7),*

$$\log_{10} x_a = \frac{-L_a}{2.303R} \cdot (1/T - 1/T_0) ,$$

where x_a *= mole fraction in solution of component crystallizing as solid phase,* T_0 *= absolute melting point of pure substance,* T *= equilibrium temperature,* R *= gas constant,* L_a *= latent heat of fusion of pure A per mole.*

VII. Table VIII records the decrease in density of a sample of NENO kept at 92.6° C. for increasing periods of time. The section concludes with an attempt to find the transition point of NENO dilatometrically (not in table form).

The eutectic temperature according to the thaw point method is approximately 75.0° C., while the melting point curves intersect at 78.5° C. The method of thermal analysis places the eutectic temperature at 78.1° C.

The composition of the eutectic mixture as indicated by the graph of the results is 5% RDX by weight.

The depression of the melting point of TNT, upon the addition of small quantities of RDX, was calculated from the van't Hoff formula $\Delta T = mK_f$ and K_f itself, the molal freezing point constant from the formula $K_f = RT^2/100\,l$ (where l is the latent heat of fusion per gram of TNT = 22.3 cal. per gm. (6)). The figures of Table II were thus obtained.

No high degree of accuracy is claimed for the above results, but it is surprising that for additions of 4 and 5% RDX, the molecular weight approaches twice the formula value (222).

The eutectic temperature lies at 55.3° C. according to the thaw point and at 60.5° C. from the intersection of the melting point curves. In accordance with this, the eutectic contains 52% by weight or 41% molar of NENO.

TABLE III (*b*)

THE SYSTEM TNT–NENO BY THE METHOD OF THERMAL ANALYSIS

Composition, wt. % NENO	Freezing point, ° C.	Eutectic temperature, ° C. (temp. of complete crystallization)
5	78.5	73.2
10	76.8	68.2
15	75.0	64.6
20	73.0	62.3
25	71.1	60.5
52	59.9	Eutectic mixture

TABLE IV

EQUILIBRIUM DATA OF THE SYSTEM NENO – DNB BY THE THAW POINT – MELTING POINT METHOD

Composition		Thaw point, ° C.	Melting point, ° C. (expt.)	Melting point, ° C.[1] (calc.)
Wt. % NENO	Mole % NENO			
0	0	88.4	89.6	—
10	5.0	57.4	86.8	86.4
20	10.6	57.2	83.2	82.6
30	16.7	56.8	77.6	78.5
40	23.8	56.5	72.8	73.2
50	32.0	56.8	67.7	66.9
60	41.4	56.8	62.6	59.7
61	42.4	56.8	62.3	—
62	43.5	56.9	61.8	—
63	44.6	56.8	63.0	—
70	52.5	57.1	68.2	68.2
80	65.4	57.2	75.6	75.6
90	81.0	57.5	82.8	82.9
100	100	89.7	90.6	—

[1] *The calculated values for the melting points were obtained by means of the Washburn and Read equation (7); the latent heat of fusion of DNB per gram = 25.4 cal. (1).*

The thaw point method and the method of thermal analysis agree fairly well in regard to the melting point, but there is great discrepancy between the two in regard to the thaw point, or temperature of eutectic melting. The solidus line as determined by Plato's method drops so gradually on the TNT side of the diagram that it does not reach the eutectic horizontal until a content of 28% NENO by weight has been attained. Such behaviour is suggestive of solid solution, implying that TNT can dissolve 28% NENO in the solid state.

TABLE V (*a*)

VELOCITY OF CRYSTALLIZATION OF TNT[1]

Temperature, °C.	Degree of supercooling, °C.	C.V.[2], mm. per min.
70.0	10.1	35
60.0	20.1	94
50.0	30.1	126
40.0	40.1	158
30.0	50.1	171
22.0	58.1	127

[1] *These values have been determined by others (2) but are reproduced here in order that they may be compared with the values for the eutectic mixture.*

[2] *The abbreviation C.V. is used throughout the tables to indicate 'crystallization velocity'.*

TABLE V (*b*)

VELOCITY OF CRYSTALLIZATION OF THE TNT – RDX EUTECTIC MIXTURE[1]

Temperature, °C.	Degree of supercooling, °C.	C.V., mm. per min.
71.2	7.3	10.7
68.7	9.8	19.1
63.0	15.5	32.4
58.0	20.5	38.7
48.0	30.5	48.6
38.0	40.5	51.2
28.0	50.5	38.2

[1] *The RDX in this mixture was previously recrystallized from acetone.*

TABLE V (*c*)

VELOCITY OF CRYSTALLIZATION OF THE TNT-RDX EUTECTIC MIXTURE IN WHICH THE RDX WAS PREVIOUSLY SIMMERED WITH WATER

Temperature, °C.	Degree of supercooling, °C.	C.V., mm. per min.
71.2	7.3	7.8
68.5	10.0	14.3
59.1	19.4	28.6
47.5	31.5	35.5
37.5	41.5	35.4
27.8	50.7	32.7

The eutectic temperature, by the thaw point method, lies at 56.9° C., while the melting point curves intersect at 61.7° C. The eutectic composition lies at 62% by weight and 44 mole % of NENO. The eutectic mixture was subjected to thermal analysis and gave a eutectic temperature of 61.2° C. The absence of any discontinuity on the cooling curve prior to the eutectic temperature confirmed the eutectic composition as 62% NENO.

TABLE VI (*a*), (*b*), (*c*), (*d*), (*e*)

SWEATING DATA FOR VARIOUS MIXTURES OF TNT–NENO

<table>
<tr><th>Time interval, hr.</th><th>% Sweated out</th><th>Time interval, hr.</th><th>% Sweated out</th><th>Time interval, hr.</th><th>% Sweated out</th></tr>
<tr><td colspan="6">VI (<i>a</i>). Composition of cartridge: 10% NENO - 90% TNT (by weight). Temperature of thermostat = 63.4° C.</td></tr>
<tr><td>0</td><td>0</td><td>146</td><td>2.78</td><td>357</td><td>3.70</td></tr>
<tr><td>24</td><td>1.85</td><td>167</td><td>2.81</td><td>406</td><td>3.70</td></tr>
<tr><td>69</td><td>2.12</td><td>238</td><td>3.34</td><td>430</td><td>3.70</td></tr>
<tr><td>94</td><td>2.41</td><td>294</td><td>3.61</td><td>—</td><td>—</td></tr>
<tr><td>118</td><td>2.68</td><td>342</td><td>3.68</td><td>—</td><td>—</td></tr>
<tr><td colspan="6">VI. (<i>b</i>). Composition of cartridge: 7% NENO - 93% TNT (by weight). Temperature of thermostat = 63.6° C.</td></tr>
<tr><td>0</td><td>0</td><td>116</td><td>2.25</td><td>285</td><td>3.22</td></tr>
<tr><td>44</td><td>1.71</td><td>164</td><td>2.78</td><td>—</td><td>—</td></tr>
<tr><td>68</td><td>1.97</td><td>237</td><td>2.98</td><td>—</td><td>—</td></tr>
<tr><td colspan="6">VI (<i>c</i>). Composition of cartridge: 5% NENO - 95% TNT (by weight). Temperature of thermostat = 63.6° C.</td></tr>
<tr><td>0</td><td>0</td><td>97</td><td>1.32</td><td>261</td><td>1.83</td></tr>
<tr><td>44</td><td>1.06</td><td>164</td><td>1.62</td><td>285</td><td>1.83</td></tr>
<tr><td>68</td><td>1.17</td><td>237</td><td>1.83</td><td>—</td><td>—</td></tr>
<tr><td colspan="6">VI (<i>d</i>). Composition of cartridge: 5% NENO - 95% TNT (by weight). Temperature of thermostat = 61.3° C.</td></tr>
<tr><td>0</td><td>0</td><td>48</td><td>0.48</td><td>168</td><td>0.48</td></tr>
<tr><td>24</td><td>0.48</td><td>96</td><td>0.48</td><td>—</td><td>—</td></tr>
</table>

VI (*e*). Thaw points and melting points of sweated extract from Tests (*a*), (*b*), (*c*), and (*d*)

Sweated material from	Thaw point, ° C.	Melting point, ° C.
(*a*)	53.8	59.2
(*b*)	55.1	59.7
(*c*)	54.8	58.8
(*d*)	55.3	59.4

TABLE VII

DENSITY DETERMINATIONS

Substance	Density of liquid gm./cc.		Density of solid gm./cc.		Contraction on cooling to 22° C., %
TNT	d_4^{85}	1.462	d_4^{22}	1.648	11.51
RDX–TNT eutectic	d_4^{85}	1.491	d_4^{22}	1.650	9.80
RDX	*		d_4^{22}	1.761	—
NENO	$d_4^{92.6}$	1.562	d_4^{22}	1.686	7.80
NENO–TNT eutectic	d_4^{61}	1.545	d_4^{22}	1.678	7.75
m-Dinitrobenzene	d_4^{90}	1.364	d_4^{22}	1.567	12.96

* *It was not possible to determine the density of liquid RDX, because of decomposition just above the melting point.*

TABLE VIII

DECREASE IN DENSITY OF MOLTEN NENO WITH TIME.
TEMPERATURE OF THERMOSTAT = 92.6° C.

Time, hr.	0	1¼	2½
Density, gm./cc.	1.562	1.561	1.559

The Transition Point of NENO

No transition point could be detected either dilatometrically or by means of the polarizing microscope. For example, a sample in a dilatometer was slowly heated to 65° C. and kept there for three days. Then it was cooled to −12° C., at which temperature it was again kept for three days. At no time was there any discontinuous movement of the xylene index.

The density determinations on the original material indicated that if two forms exist, the original material was the β-form. This was caused to transform to the α-form by stirring a suspension in chloroform. The densities of the untreated and treated material were as follows:

(*a*) Untreated NENO; $d_4^{22} = 1.686$ gm./cc.

(*b*) NENO stirred in chloroform for fifteen hours: $d_4^{22} = 1.706$ gm./cc.

Discussion of Results

(*a*) *The System: TNT–RDX*

The equilibrium data for this system give rise to two smooth curves intersecting at the eutectic: there is no indication of compound formation. It is surprising, however, that the addition of 5% RDX depresses the freezing point of TNT by only 1.5° C. This could be explained as due to the formation of solid solutions of RDX in TNT, but this is doubtful in view of the constancy of the thaw point for mixtures containing as little as 2% RDX. On the other hand, it is quite possible that the solute RDX is associated in solution in liquid TNT. The apparently high molecular weight of RDX as calculated from the freezing point depression in Table II tends to support this, but no high degree of accuracy is claimed for these results.

The eutectic temperature as determined by the intersection of the melting point curves (78.5° C.) is in good agreement with direct determination of the eutectic temperature from the cooling curves, viz., 78.1° C., but both these values are about three degrees higher than the thawing temperature. The discrepancy is due to the presence of impurities.

The velocity of crystallization of the TNT–RDX eutectic mixture was determined on two different preparations, using RDX that had been treated differently in the two cases. Table V shows that there is a marked difference in crystallization velocity depending on whether the RDX has been recrystallized from acetone or simmered with distilled water. The crystallization velocity of the former sample was considerably greater, indicating that RDX that has been merely simmered with water contains impurities that are removed by recrystallization from acetone. The presence of 5% RDX reduces the crystallization velocity of TNT to about one-third. Although the magnitude of the reduction is considerable for so small an addition of the second substance, the general behaviour confirms the observation of Moore (4) that the addition of a second component tends to reduce the crystallization velocity of the original material. Finally, both eutectic mixtures exhibit a maximum crystallization velocity, at about 35° to 40° C. of supercooling, in accordance with Tammann's finding (3), but there is no evidence of a region of constant crystallization velocity; the curve rises to a maximum and then falls immediately.

(*b*) *The System TNT–NENO*

The equilibrium diagram for this system also shows no evidence of compound formation. Again the melting point curves are both smooth and they intersect at a temperature of 60.5° C. and at a composition of 52% by weight or 41% molar of NENO. The eutectic temperature by thermal analysis is 59.9° C. The thaw point line again falls below the above values: it lies at 55.3° C. The cause of the discrepancy is the same as in the system TNT–RDX, viz., impure materials.

When the results of both thermal analysis and thaw point method are plotted, it is at once apparent that the eutectic temperature is not reached by any mixture until a content of 20 to 30% NENO is reached. This suggests the possibility of solid solutions. To test this hypothesis, 'sweating' experiments were conducted as described under "Apparatus". Contrary to expectations, a 5% NENO, 95% TNT cartridge lost liquid matter even at 61.3° C., at a temperature 2.7° C. below the supposed solidus line, where no sweating was expected. Moreover, the amount of material exuded decreased as the eutectic temperature of 60.5° C. was approached. This eliminates the possibility of the formation of solid solution.

Examination of the sweating data of Table VI (*a*), (*b*), (*c*), (*d*), (*e*), shows that the amount of liquid exuded is far less than that calculated from the eutectic composition. The reason probably is that a great deal of the melting eutectic is retained within the cavities of the cartridge and only a small portion actually drops away. The thermal analyses in Table VI (*e*) corroborate the eutectic composition of the various sweated extracts.

The theoretical melting points calculated by the equation of Washburn and Read (7) are in fair agreement with the experimentally determined melting points.

(*c*) *The System: TNT–Dinitrobenzene*

In this system the same discrepancy, as before, was encountered in the determination of the eutectic temperature. The melting point curves intersect at 61.7° C., while the eutectic halt lies at 61.2° C. The thaw point horizontal again lies below these two values at 56.9° C. The theoretical values of the melting point as determined from the equation of Washburn and Read agree fairly well with the experimental values.

(*d*) *The Stability of NENO*

The tendency of molten NENO to decompose was confirmed both visually and quantitatively. Table VIII shows that at only 2.0° C. above its melting point there was a decrease in density of 0.001 gm. per cc. at the end of one and one-half hours. After two and one-half hours the decomposition became more pronounced. Qualitatively, bubbles of gas could be observed in the melt at the end of one hour.

(*e*) *Transition Point of NENO*

The transition point of NENO could not be established dilatometrically, although the densities of the samples of NENO before and after treatment with chloroform indicate that an α- and a β-form do exist. It required, however, 15 hr. stirring in chloroform to convert the β-form to the α-form: five hours' stirring had little or no effect. The α-form had a density of 1.706 gm. per cc.

(*f*) *Densities*

The density determinations (Table VII) show that the contractions of the eutectic mixtures on solidifying are in all cases less than those of the pure components. It has already been pointed out that a diminished contraction is a desirable characteristic from the point of view of shell filling.

Conclusion

As this work was dicatated by war exigencies, it cannot be claimed that any systematic scheme has been pursued or definite conclusion arrived at. We feel, however, that these extensive data, disconnected as they are, cannot be without interest to future workers with the new explosives RDX and NENO.

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A METHOD OF ANALYSIS FOR THE SYSTEM: BENZENE - ETHYL ALCOHOL - CARBON TETRACHLORIDE[1]

BY A. N. CAMPBELL[2] AND S. I. MILLER[3]

Abstract

The densities and refractive indices (N_c) of binary and ternary mixtures of benzene, ethyl alcohol, and carbon tetrachloride have been determined at 25° C. From these data, a method for the analysis of ternary liquid mixtures of these components has been developed. The limit of accuracy in the analysis of ternary mixtures of the pure components is 0.3%. The method can be applied to the analysis of commercial materials with an accuracy of 2.0%.

Introduction

The subject matter of this paper represents a preliminary step in the study of the isobaric distillation of the ternary mixture named in the title. In order to determine the compositions of equilibrium liquid and vapour phases a rapid and accurate method of analysis was required. Any chemical analysis would have been protracted and inaccurate, even if it were possible. We were therefore obliged to use purely physical methods.

Benzene, ethyl alcohol, and carbon tetrachloride are miscible in all proportions, and, just as one physical property is sufficient to fix the composition of a binary mixture, two will determine the composition of a ternary. We chose refractive index and density as suitable properties, since they can be determined readily and accurately on relatively small quantities of liquid (10 cc.): this was a necessary condition for our work since the quantity of condensed vapour was necessarily small. The method is not new: Barbaudy (1) analysed in this manner ternary mixtures of benzene, alcohol, and water, with an accuracy of 0.25%. We claim an accuracy of 0.2%, a high degree of accuracy for the analysis of an organic system.

Obviously, prior to the analysis of any particular system, a complete calibration must be carried out, i.e., the densities and refractive indices must be determined over the complete range of mixtures, the composition being known.

Previous Investigations

(a) *Benzene–Alcohol*

Barbaudy (1), studying the ternary system benzene - alcohol - water, determined the densities and refractive indices (N_D) at 25° C. Other workers (11, 16), whose results were not available, have supplied similar data at other temperatures.

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Contribution from the Department of Chemistry, The University of Manitoba, Winnipeg, Man.

[2] *Professor of Chemistry and Head of Department.*

[3] *Holder of a Bursary under the National Research Council of Canada, 1945-1946.*

The majority of Barbaudy's density values coincide with our experimental curve given in Fig. 1. His figures for refractive index (N_D) generally parallel those for N_c obtained by us (Fig. 2).

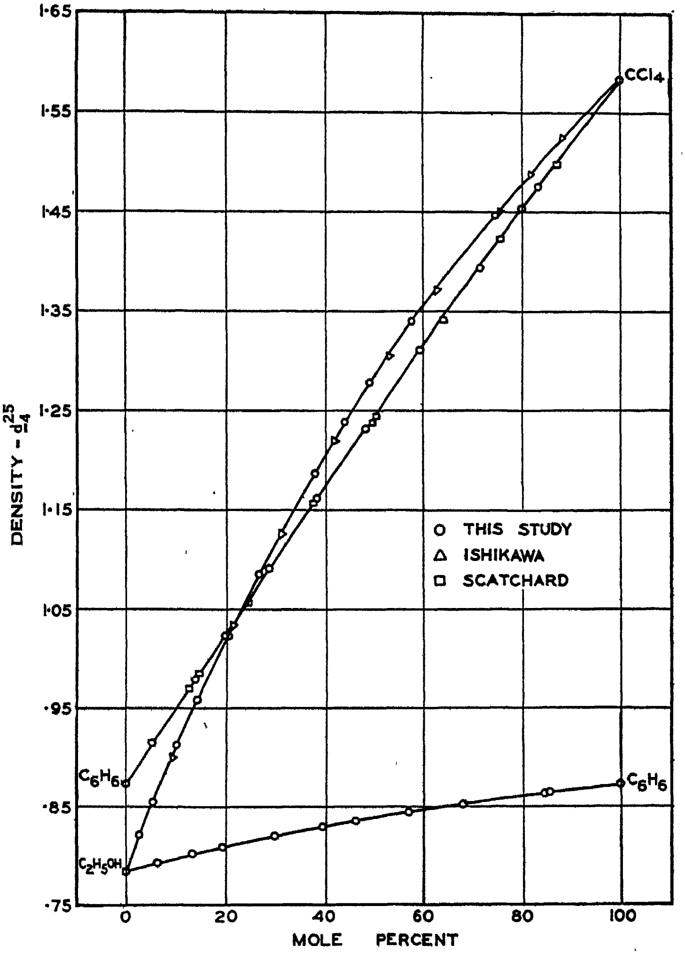

FIG. 1. *The binary systems—previous investigations—*d_4^{25}.

(b) Carbon Tetrachloride–Alcohol

King and Smedley (10) determined densities for this binary very crudely. Ishikawa and Yamaguchi (9) determined the densities and used them for purposes of analysis. The density of their alcohol indicates a small water content of 0.3%, while their carbon tetrachloride also differs slightly from the material used in this study. Nevertheless, Fig. 1 shows that these small deviations affect but little the comparison between their work and ours.

Curtis and Titus (5) determined densities and refractive indices (N_D) at 19.4° C., as a part of their study of the ternary system carbon tetrachloride – alcohol – water. Their refractive index curve runs parallel to ours for N_c.

(*c*) *Benzene – Carbon Tetrachloride*

Brown (3, 4) found densities for this binary mixture at 20° C. In a similar study, Wood and Brusie (22) evaluated thermodynamic functions from density–composition results at 30° C.

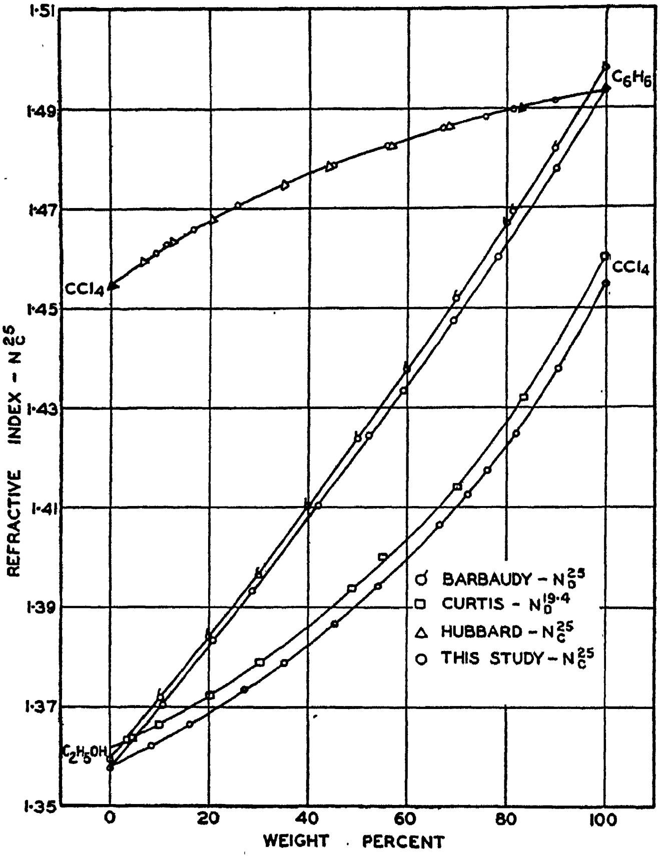

Fig. 2. *The binary systems—previous investigations—N_c^{25}.*

Rosanoff (17) and Zawidzki (23) determined the refractive indices at 25.2° C., for purposes of analysis.

McMillan and McDonald (13) found densities at 27° C. and refractive indices (N_D) at 25° C. They do not claim more than 1.0% precision: moreover the properties of their materials indicate substantial amounts of impurity.

Scatchard, Wood, and Mochel (18) determined densities at 25° C. Their values are compared with ours in Fig. 1.

Hubbard's results (7, 8) for densities and refractive indices (N_D, N_c, etc.) of various binary systems, including benzene – carbon tetrachloride, are quoted in International Critical Tables. His N_c data are compared with ours in Fig. 2.

Experimental

PURIFICATION OF MATERIALS

Benzene

B.D.H. 'Analar' benzene was used, without further purification. This material is so good, as revealed by its density and refractive index, that attempted purification could not have improved it.

Carbon Tetrachloride

'Analar' carbon tetrachloride was fractionally distilled over phosphorus pentoxide, and the fraction distilling within a 0.2° C. range used.

Ethyl Alcohol

The ordinary concentrated alcohol of commerce (6% water) was refluxed with 12 *N* sulphuric acid and distilled. The middle distillate was treated with sodium hydroxide and silver nitrate, refluxed, and distilled, the middle distillate only being collected. This distillate was then treated with several successive portions of lime, which had been calcined at 1000° C. After standing for several days over lime, this alcohol was decanted, refluxed with fresh lime, and fractionated.

The first and last fractions were rejected and the alcohol collected over a 0.2° C. range. This alcohol had a water content of less than 0.07%, judging from its density.

Published properties of 'pure' materials differ, indicating frequently that the materials used were not really pure. The best figure for the density of alcohol is that determined at the Bureau of Standards by Osborne, McKelvey and Bearce (15). Table I reveals the differences in the properties of materials used by various workers.

TABLE I

PURITY OF MATERIALS

Source	Benzene			Ethyl alcohol			Carbon tetrachloride		
	d_4^{25}	N_c^{25}	N_D^{25}	d_4^{25}	N_c^{25}	N_D^{25}	d_4^{25}	N_c^{25}	N_D^{25}
This study	0.87376	1.49331	1.49797	0.78524	1.35767		1.58455	1.45478	
Ishikawa (9)				0.7860			1.5842		
Barbaudy (1)	0.87363		1.49795	0.78506		1.3592			
Scatchard (18)	0.87370						1.58426		
McMillan (13)	$0.8734^{27°}$		1.4985				$1.5866^{27°}$		1.4549
Osborne (15)				0.78506					
Martin (14)	0.87288	1.49312							
Hubbard (7, 8)	0.87372	1.49330	1.49794				1.58456	1.45464	1.45732
Varteressian (21)	0.8727		1.4976	0.7852		1.3598			

PROCEDURE

Temperature Control

The temperature of the thermostat was 25.0° ± 0.03° C. Thermostat water circulated around the refractometer gave a temperature of 25.0° ± 0.05° C.

Preparation of Mixtures

When the components are volatile, it is not so easy to prepare a mixture of accurately known composition. We prepared our mixture by weighing in 100 cc. long-necked, glass stoppered flasks. Such weights of components were chosen that the flask was always filled into the narrow neck, in order to reduce change of composition by volatilization. Weighings to six, sometimes five, significant figures were usual. Percentage compositions are listed to four figures, although three figures are sufficient for the attainable accuracy of analysis. The following factors lead to uncertainty in the fourth figure: (i) omission of buoyancy correction; (ii) leakage at ground glass stoppers; (iii) evaporation on opening flasks or transferring liquids. These errors are to some extent compensatory, and the composition figures are accurate to better than 0.1%.

Refractive Index Measurements

A Pulfrich refractometer was used, with water circulation at 25° C. The H_c line of the hydrogen discharge tube was used for the measurements.

Prolonged observations gave drifting readings, because of a slow fractional distillation from the liquid in the cell. Therefore the cell and the liquid mixture, in a separate stoppered container, were both brought to 25° C. before filling the cell of the refractometer.

Density Determinations

For such volatile mixtures as these, we found the Weld specific gravity bottle best. This pycnometer has a ground glass cap that reduces evaporation to a minimum. As with the determinations of refractive index, the mixture was first brought to 25° C. in stoppered containers in the thermostat before filling the pycnometer.

Since our results were to be used directly in analysis, the weights of liquid and of calibrating water held by the pycnometer were not corrected for buoyancy. Since the bottles were counterpoised, variation in buoyancy did not affect the results. Nevertheless, it should be noted that not all the densities of this paper are corrected to vacuum. Wherever a comparison between our results and those of other workers is made, this correction has been introduced, e.g., in Fig. 1. The symbol $\underline{d}_4^t$ is used for corrected density, and d_4^t for uncorrected. To convert the densities given in this paper to vacuum or absolute densities, a table (Table II) of correction factors is supplied.

Experimental Results

The experimental results follow in tables. Since the direct determinations of density and refractive index were exceedingly numerous (there were about 250 such), they are not given in this paper. Instead of this, Tables III and IV give the isodensity and isofract data. These were obtained by plotting the experimental data for each pseudobinary system as a family of curves and drawing lines of equal density and equal refractive index through them.

At the top of each column in Tables III and IV are given the fixed ratios of the pseudobinaries. From these data the triangular diagram of Fig. 7 was obtained. The other tables are explained under Discussion.

TABLE II

CORRECTIONS FOR ANALYTIC DENSITIES, d_4^{25}, TO VACUUM d_4^{25}

Over 1.55	−0.0007	1.12 –1.25	−0.0002
1.45–1.55	−0.0006	1.04 –1.12	−0.0001
1.36–1.45	−0.0005	0.955–1.04	0.0000
1.29–1.36	−0.0004	0.870–0.955	+0.0001
1.25–1.29	−0.0003	0.785–0.870	+0.0002

Discussion of Results

(a) *Experimental Curves*

An orderly method of obtaining and assembling data in ternary systems is afforded by the use of pseudobinary curves. Schreinemakers (19, 20), for example, used this method of tabulating his vapour pressure data. It consists simply in adding to a fixed binary mixture varying amounts of the third component. If the binary mixture is treated as one component, it is possible to plot any property against composition on a rectilinear diagram. Figs. 3 to 6 express the experimental results, as determined directly.

Ternary mixtures were made up of binary mixtures of benzene–alcohol or carbon tetrachloride–alcohol to which carbon tetrachloride or benzene, respectively were added. In Fig. 3, for example, the figures on the left represent the percentage of benzene in the binary, benzene–alcohol. To each of these, carbon tetrachloride was added, giving rise to isothermal density–composition curves, all of which end at the density of pure carbon tetrachloride. Fig. 4 gives curves of refractive index for the same mixtures. Figs. 5 and 6 are analogous, the initial binary being carbon tetrachloride–alcohol. (In Fig. 5, in order to separate the curves, each curve has the indicated scale moved vertically by a multiple of 0.0100 density units: all curves should coincide at the density of pure carbon tetrachloride, for 100% carbon tetrachloride.)

Theoretically, one binary mixture, e.g., alcohol–benzene, should be sufficient to give all the required data, but one binary set supplements the other in regions where data are scanty, although considerable overlapping does occur in the central portions of Figs. 4 and 6. This will be more obvious when Fig. 7 is discussed.

(b) *Calibration Diagram*

Fig. 7 scaled down from the actual calibration diagram is based on points taken from the experimental curves. Lines running from the base upwards are lines of constant density, isodensity lines: lines sloping generally from the left side to the base are lines of constant refractive index, isofracts (Bowen (2)). The triangular diagram was constructed as follows. Horizontals, cutting the rectangular experimental curves in Figs. 3 to 6 gave sets of composition data corresponding to constant densities (Table III) and constant refractive indices (Table IV). Every sequence obtained for a constant density from Figs. 3 and 5 gave an isodensity line in Fig. 7; every sequence obtained from Figs. 4 and 6 for a constant refractive index gave an isofract in Fig. 7.

TABLE III (*a*)

DERIVED ISODENSITY DATA

$\frac{CCl_4}{C_2H_5OH}$	$\frac{0}{100}$	$\frac{8.76}{91.24}$	$\frac{16.45}{83.55}$	$\frac{27.32}{72.68}$	$\frac{35.57}{64.43}$	$\frac{45.81}{54.19}$	$\frac{54.44}{45.56}$	$\frac{66.9}{33.1}$	$\frac{72.36}{27.64}$	$\frac{82.09}{17.91}$	$\frac{90.73}{9.27}$	$\frac{100}{0}$
d_4^{25}	Per cent C_6H_6 in ternary											
0.800	18.00	—	—	—	—	—	—	—	—	—	—	—
0.820	41.72	—	—	—	—	—	—	—	—	—	—	—
0.840	64.70	36.80	—	—	—	—	—	—	—	—	—	—
0.860	87.04	76.90	24.10	—	—	—	—	—	—	—	—	—
0.880	—	—	—	80.30	90.90	94.36	95.78	97.12	97.50	97.98	98.04	98.38
0.900	—	—	—	27.40	64.16	78.87	84.22	88.48	89.77	91.44	92.46	93.37
0.920	—	—	—	—	40.90	64.18	73.17	80.34	82.42	85.30	87.12	88.73
0.940	—	—	—	—	19.00	50.22	62.92	72.53	75.46	79.42	82.00	84.17
0.960	—	—	—	—	—	36.98	52.98	65.08	68.83	73.81	77.08	79.77
0.980	—	—	—	—	—	24.33	43.20	58.00	62.46	68.44	72.40	75.62
1.000	—	—	—	—	—	12.20	33.68	51.23	56.48	63.36	67.86	71.68
1.020	—	—	—	—	—	1.16	24.62	44.80	50.70	58.42	63.52	67.93
1.040	—	—	—	—	—	—	16.23	38.68	45.13	53.67	59.37	64.36
1.060	—	—	—	—	—	—	8.23	32.78	39.74	49.14	55.37	60.98
1.080	—	—	—	—	—	—	1.28	27.00	34.58	44.78	51.53	57.68
1.100	—	—	—	—	—	—	—	21.44	29.60	40.57	47.82	54.53
1.120	—	—	—	—	—	—	—	16.10	24.80	36.56	44.27	51.42
1.140	—	—	—	—	—	—	—	11.02	20.19	32.63	40.90	48.38
1.160	—	—	—	—	—	—	—	6.23	15.78	28.79	37.61	45.46
1.180	—	—	—	—	—	—	—	1.47	11.46	25.13	34.43	42.42
1.200	—	—	—	—	—	—	—	—	7.40	21.60	31.37	39.56
1.220	—	—	—	—	—	—	—	—	3.37	18.23	28.30	36.77
1.240	—	—	—	—	—	—	—	—	—	14.98	25.32	34.12
1.260	—	—	—	—	—	—	—	—	—	11.74	22.44	31.60
1.280	—	—	—	—	—	—	—	—	—	8.62	19.94	29.21
1.300	—	—	—	—	—	—	—	—	—	5.73	17.66	26.87
1.320	—	—	—	—	—	—	—	—	—	2.86	14.47	24.62
1.340	—	—	—	—	—	—	—	—	—	0.03	12.03	22.42
1.360	—	—	—	—	—	—	—	—	—	—	9.63	20.33
1.380	—	—	—	—	—	—	—	—	—	—	7.36	18.22
1.400	—	—	—	—	—	—	—	—	—	—	5.12	16.22
1.420	—	—	—	—	—	—	—	—	—	—	2.93	14.30
1.440	—	—	—	—	—	—	—	—	—	—	0.76	12.42
1.460	—	—	—	—	—	—	—	—	—	—	—	10.52
1.480	—	—	—	—	—	—	—	—	—	—	—	8.73
1.500	—	—	—	—	—	—	—	—	—	—	—	6.98
1.520	—	—	—	—	—	—	—	—	—	—	—	5.29
1.540	—	—	—	—	—	—	—	—	—	—	—	3.63
1.560	—	—	—	—	—	—	—	—	—	—	—	2.04
1.580	—	—	—	—	—	—	—	—	—	—	—	0.42

Each of the experimental curves in Figs. 3 to 6 had two components in a fixed weight ratio. These fixed ratios of composition are represented by the fainter lines originating from the benzene and carbon tetrachloride corners in Fig. 7. All derived data fall on these lines, and indeed, the drawing up of the triangular analysis diagram is greatly simplified if these lines are drawn in first.

TABLE III (*b*)

DERIVED ISODENSITY DATA

$\frac{C_6H_6}{C_2H_5OH}$	$\frac{0}{100}$	$\frac{10.69}{89.31}$	$\frac{21.01}{78.99}$	$\frac{28.94}{71.06}$	$\frac{42.05}{57.95}$	$\frac{52.55}{47.45}$	$\frac{59.26}{40.74}$	$\frac{69.30}{30.70}$	$\frac{78.38}{21.62}$	$\frac{90.28}{9.72}$
d_4^{25}	Per cent CCl_4 in ternary									
0.800	3.54	1.47	—	—	—	—	—	—	—	—
0.820	8.24	6.23	4.16	2.53	—	—	—	—	—	—
0.840	12.79	10.88	8.92	7.32	4.66	2.53	1.13	—	—	—
0.860	17.14	15.40	13.53	12.00	9.40	7.24	5.92	3.99	1.97	—
0.880	21.21	19.63	17.93	16.45	14.00	11.93	10.60	8.78	6.77	4.07
0.900	25.12	23.42	22.01	20.58	18.38	16.44	15.22	13.40	11.57	8.93
0.920	28.94	27.18	25.97	24.46	22.57	20.79	19.53	17.78	16.06	13.60
0.940	32.53	30.79	29.73	28.28	26.50	24.58	23.66	21.90	20.30	18.03
0.960	35.96	34.33	33.33	32.00	30.27	28.30	27.56	25.87	24.38	22.24
0.980	39.27	37.66	36.77	35.62	33.87	31.99	31.30	29.64	28.33	26.14
1.000	42.42	40.69	40.02	39.03	37.34	35.52	34.96	33.37	32.06	30.00
1.020	45.42	43.70	43.12	42.30	40.63	38.98	38.37	36.98	35.67	33.70
1.040	48.27	46.66	46.20	45.46	43.82	42.25	41.66	40.46	39.11	37.34
1.060	51.10	49.57	49.21	48.48	46.88	45.46	44.86	43.78	42.38	40.74
1.080	53.86	52.41	51.97	51.37	49.93	48.56	47.97	46.87	45.62	44.06
1.100	56.54	55.18	54.66	54.13	52.75	51.47	50.96	49.90	48.75	47.24
1.120	59.13	57.80	57.26	56.61	55.54	54.38	53.78	52.80	51.76	50.36
1.140	61.56	60.32	59.81	59.17	58.21	57.12	56.38	55.64	54.67	53.37
1.160	63.94	62.68	62.24	61.64	60.80	59.80	59.30	58.42	57.53	56.23
1.180	66.23	65.03	64.64	64.12	63.24	62.40	61.76	61.03	60.20	58.47
1.200	68.43	67.33	66.98	66.55	65.67	64.82	64.23	63.56	62.60	61.68
1.220	70.58	69.58	69.24	68.82	68.00	67.19	66.68	66.06	65.82	64.24
1.240	72.63	71.70	71.44	71.03	70.23	69.52	69.08	68.43	67.43	66.78
1.260	74.64	73.74	73.53	73.20	72.42	71.78	71.38	70.71	69.74	69.21
1.280	76.59	75.75	75.54	75.27	74.58	73.99	73.57	72.98	72.06	71.54
1.300	78.46	77.68	77.56	77.27	76.62	76.08	75.67	75.06	74.36	73.78
1.320	80.36	79.59	79.43	79.18	78.66	78.17	77.78	77.13	76.54	75.99
1.340	82.10	81.40	81.32	81.07	80.63	80.17	79.77	79.17	78.64	78.17
1.360	83.83	83.20	83.15	82.90	82.51	82.12	81.67	81.18	80.73	80.22
1.380	85.53	84.95	84.91	84.67	84.33	84.00	83.58	83.09	82.73	82.25
1.400	87.16	86.67	86.58	86.42	86.06	85.79	85.46	85.00	84.63	84.21
1.420	88.72	88.37	88.24	88.03	87.80	87.50	87.23	86.80	86.54	86.13
1.440	90.22	89.99	89.83	89.70	89.52	89.21	88.98	88.62	88.31	87.99
1.460	91.70	91.57	91.37	91.26	91.20	90.86	90.63	90.36	90.20	89.78
1.480	93.15	93.01	92.87	92.77	92.71	92.46	92.26	92.00	91.89	91.54
1.500	94.54	94.44	94.34	94.23	94.19	94.02	93.83	93.61	93.56	93.25
1.520	95.86	95.83	95.73	95.66	95.64	95.55	95.35	95.20	95.14	94.88
1.540	97.18	97.17	97.07	97.04	97.02	96.97	96.81	96.73	96.66	96.47
1.560	98.42	98.43	98.37	98.37	98.37	98.36	98.29	98.20	98.15	98.04
1.580	99.62	—	—	—	—	—	—	—	—	99.54

TABLE IV (*a*)

DERIVED ISOFRACT DATA

$\frac{CCl_4}{C_2H_5OH}$	$\frac{0}{100}$	$\frac{8.76}{91.24}$	$\frac{16.45}{83.55}$	$\frac{27.32}{72.68}$	$\frac{35.57}{64.43}$	$\frac{45.81}{54.19}$	$\frac{54.44}{45.56}$	$\frac{66.9}{33.1}$	$\frac{72.36}{27.64}$	$\frac{82.09}{17.91}$	$\frac{90.73}{9.27}$	$\frac{100}{0}$
N_c^{25}	Per cent C_6H_6 in ternary											
1.360	1.93	—	—	—	—	—	—	—	—	—	—	—
1.365	6.17	2.54	—	—	—	—	—	—	—	—	—	—
1.370	10.34	6.66	3.06	—	—	—	—	—	—	—	—	—
1.375	14.38	10.73	7.14	1.49	—	—	—	—	—	—	—	—
1.380	18.42	14.83	11.22	5.66	0.94	—	—	—	—	—	—	—
1.385	22.43	18.83	15.26	9.82	5.03	—	—	—	—	—	—	—
1.390	26.38	22.82	19.39	13.99	9.22	2.84	—	—	—	—	—	—
1.395	30.25	26.77	23.57	18.16	13.51	7.01	0.65	—	—	—	—	—
1.400	34.18	30.62	27.70	22.21	17.66	11.30	4.67	—	—	—	—	—
1.405	38.07	34.64	31.76	26.35	21.94	15.60	8.66	—	—	—	—	—
1.410	41.90	38.57	35.78	30.56	26.14	19.92	13.16	3.32	—	—	—	—
1.415	45.67	42.52	39.73	34.76	30.40	24.22	17.68	7.80	2.23	—	—	—
1.420	49.42	46.42	43.76	38.94	34.73	28.60	22.24	12.40	6.88	—	—	—
1.425	53.14	50.26	47.78	43.15	39.08	33.13	26.82	17.16	11.63	0.23	—	—
1.430	56.83	54.05	51.78	47.32	43.48	37.70	31.66	22.02	16.68	5.03	—	—
1.435	60.48	57.83	55.72	51.42	47.80	42.41	37.74	27.08	21.88	10.16	—	—
1.440	64.10	61.70	59.62	55.53	52.17	47.07	41.81	32.46	27.26	15.62	2.52	—
1.445	67.63	65.47	63.48	59.66	56.53	51.82	46.90	37.95	32.83	21.40	8.06	—
1.450	71.17	69.24	67.23	63.82	60.90	56.62	52.08	43.50	38.62	27.60	14.16	—
1.455	74.67	72.96	71.18	67.98	65.33	61.50	57.28	49.37	44.63	34.02	20.98	0.28
1.460	78.16	76.60	75.07	72.18	69.88	66.33	62.47	55.24	51.00	40.79	28.48	7.18
1.465	81.56	80.26	78.97	76.55	74.37	71.21	67.73	61.40	57.48	48.00	36.30	15.13
1.470	84.96	83.80	82.77	80.83	78.93	76.13	73.20	67.63	64.24	55.67	44.84	24.73
1.475	88.34	87.46	86.53	85.01	83.42	81.12	78.77	74.18	71.41	64.73	54.28	35.58
1.480	91.62	91.01	90.06	89.14	87.96	86.22	84.43	81.01	78.96	73.50	64.82	49.13
1.485	94.76	94.40	93.96	93.24	92.43	91.36	90.18	88.03	86.69	82.94	76.98	64.19
1.490	97.83	97.74	97.58	97.27	96.88	96.54	96.00	95.20	94.63	91.98	89.77	83.52

TABLE IV (*b*)

DERIVED ISOFRACT DATA

$\frac{C_6H_6}{C_2H_5OH}$	$\frac{0}{100}$	$\frac{10.69}{89.31}$	$\frac{21.01}{78.99}$	$\frac{28.94}{71.06}$	$\frac{42.05}{57.95}$	$\frac{52.55}{47.45}$	$\frac{59.26}{40.74}$	$\frac{69.30}{30.70}$	$\frac{78.38}{21.62}$	$\frac{90.28}{9.72}$
N_c^{25}	Per cent CCl_4 in ternary									
1.360	4.81	—	—	—	—	—	—	—	—	—
1.365	14.18	—	—	—	—	—	—	—	—	—
1.370	22.47	—	—	—	—	—	—	—	—	—
1.375	30.10	9.81	—	—	—	—	—	—	—	—
1.380	37.18	20.07	—	—	—	—	—	—	—	—
1.385	43.77	29.84	4.91	—	—	—	—	—	—	—
1.390	49.83	38.60	16.87	—	—	—	—	—	—	—
1.395	55.42	45.87	27.58	5.54	—	—	—	—	—	—
1.400	60.66	52.48	37.20	19.39	—	—	—	—	—	—
1.405	65.63	58.54	46.00	31.58	—	—	—	—	—	—
1.410	70.22	64.16	53.88	42.23	—	—	—	—	—	—
1.415	74.43	69.36	60.88	51.48	18.28	—	—	—	—	—
1.420	78.46	74.18	67.53	59.83	34.38	—	—	—	—	—
1.425	82.20	78.68	73.48	67.44	48.58	5.00	—	—	—	—
1.430	85.68	82.88	79.01	74.56	59.99	29.40	—	—	—	—
1.435	89.00	86.83	83.96	80.92	70.08	48.90	12.60	—	—	—
1.440	92.02	90.47	88.48	86.56	79.61	66.24	44.38	—	—	—
1.445	94.83	93.86	92.70	91.63	87.77	80.06	67.84	—	—	—
1.450	97.47	97.03	96.58	96.12	94.48	91.48	87.33	45.90	—	—
1.455	—	—	—	—	—	—	—	—	98.40	99.47
1.460	—	—	—	—	—	—	—	—	17.70	87.17
1.465	—	—	—	—	—	—	—	—	—	72.66
1.470	—	—	—	—	—	—	—	—	—	51.84
1.475	—	—	—	—	—	—	—	—	—	23.07

The angle of intersection of the two sets of iso-lines averages about 60°. Had this angle been close to a right angle, the maximum precision of analysis would have been possible. On the other hand, had this angle been close to 0° (parallel line) or had a double intersection occurred (excessive curvature in one set), the analysis would have been impossible. As it is, and using a triangle with sides almost 3 ft. in length, and a criss-cross grid of iso-lines, the analysis is very satisfactory.

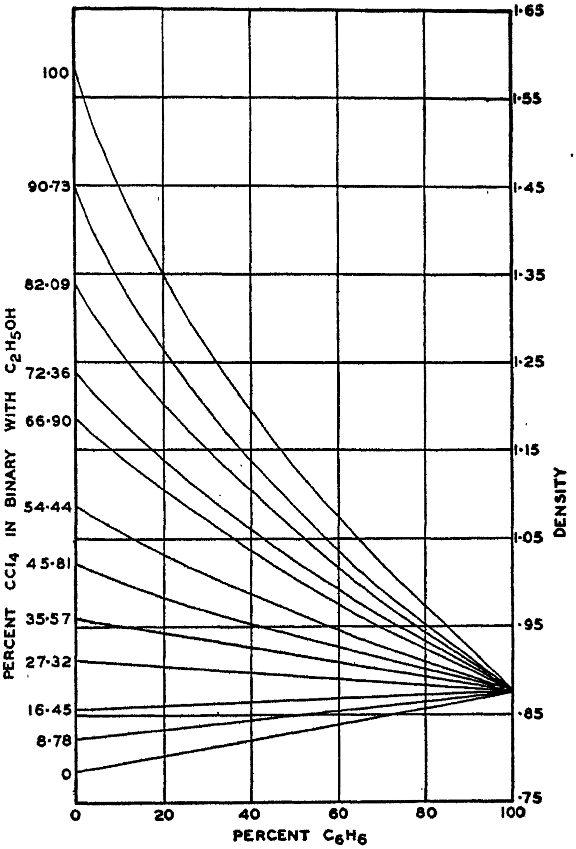

FIG. 3. *Experimental curves*—d_4^{25}.

The use of the triangular diagram for analysis is simple. Any ternary mixture will have a refractive index and a density lying on the diagram between two isofracts and two isodensity lines. These known properties, lying on interpolated lines, will intersect at a unique point giving the composition of the unknown mixture.

Although we claim only 0.3% accuracy, the analysis is usually better than 0.2% of the total for each component. The following mixtures, weighed out at random, were used to test the attainable accuracy. Compositions obtained

TABLE V

ACCURACY OF THE ANALYTIC DIAGRAM

No.	——	d_4^{25}	N_c	% C_6H_6	% C_2H_5OH	% CCl_4	Maximum deviations, %
1	Weighed		1.45088	71.83	28.17	0	
	Derived			71.85	28.15		0.02
2	Weighed	1.41033		15.20	0	84.80	
	Derived.			15.15		84.85	0.05
3	Weighed	1.0610	1.43074	26.32	27.39	46.29	
	Derived			26.3	27.3	46.4	0.11
4	Weighed	0.9124	1.45548	63.77	21.24	14.99	
	Derived			63.8	21.1	15.1	0.15
5	Weighed	0.8824	1.47643	85.07	9.99	4.94	
	Derived			85.1	9.95	4.95	0.03
6	Weighed	1.4425	1.44606	4.37	6.13	89.50	
	Derived			4.2	6.3	89.5	0.17
7	Weighed	1.1859	1.44103	20.50	16.55	62.95	
	Derived			20.70	16.35	62.95	0.20
8	Weighed	0.8413	1.37174	6.03	82.10	11.88	
	Derived			6.2	82.0	11.8	0.17
9	Weighed	0.8108	1.36779	6.08	88.92	5.00	
	Derived			6.3	88.9	4.8	0.22

from the diagram, i.e., from the physical properties, are termed 'derived', as contrasted with the actual or 'weighed' figures.

The analysis is most accurate where the isodensity and isofract lines are close together. In general, where the isodensity lines are widely spread, the isofracts are close together and vice versa. The alcohol corner is the least covered and therefore the least accurate. Analyses in this region will be sensibly affected by errors of 0.00010 unit in either density or refractive index.

Applications

Analysis of Commercial Materials

The use of the analysis diagram for so-called 'practical' or 'stock' materials of industry deserves brief discussion. Table VI lists the properties of commercial materials, together with their deviations from those of the pure materials of this study, while Table VII compares weighed with derived compositions in a single case. The method here is first to find the approximate compositions from the known density and refractive index, assuming that the mixture is of pure components, then to apply a correction to observed density and refractive index, derived from the mixture rule, the deviations of the impure components, and the approximate proportions.

TABLE VI

PROPERTIES OF COMMERCIAL MATERIALS

Component	d_4^{25}	Deviation	N_c^{25}	Deviation
B.D.H. Technical benzene	0.8732	−0.0004	1.49300	−0.00031
Eastman's Practical carbon tetrachloride	1.5848	−0.0004	1.45458	−0.00020
Alcohol (1.7% water)	0.7902	+0.0052	1.35847	−0.00080

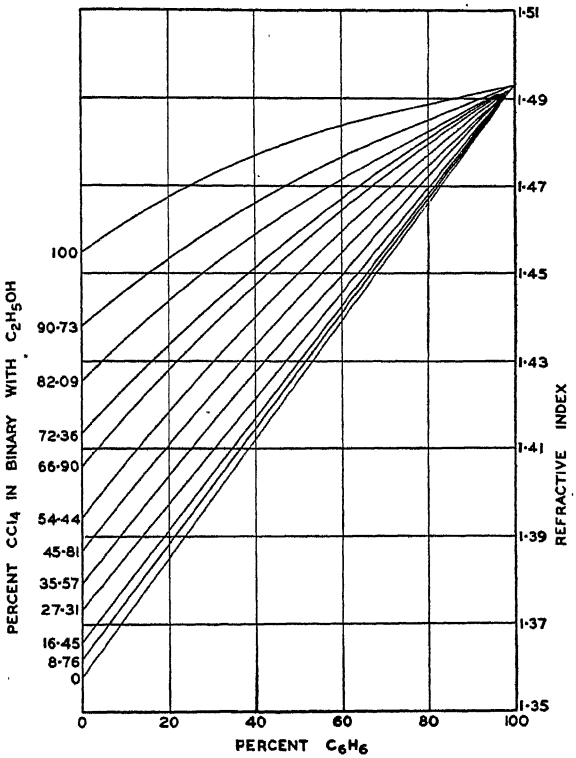

FIG. 4. *Experimental curves*—N_c^{25}.

TABLE VII

ANALYSIS OF A COMMERCIAL MIXTURE

—	d_4^{25}	d_4^{25} (corr.)	N_c^{25}	N_c(corr.)	% C_6H_6	% C_2H_5OH	% CCl_4
Weighed	1.0061		1.45009		45.7	19.9	34.4
Derived		1.0053		1.45046	46.4	19.3	34.3

The maximum error in the above analysis was 0.7%. The error will naturally depend on the purity of the components. Although a thorough survey of every region of the diagram was not made, it is probable that the above materials in ternary mixtures could be analysed to well within 2.0%. This is fair accuracy and industrial application is at least conceivable.

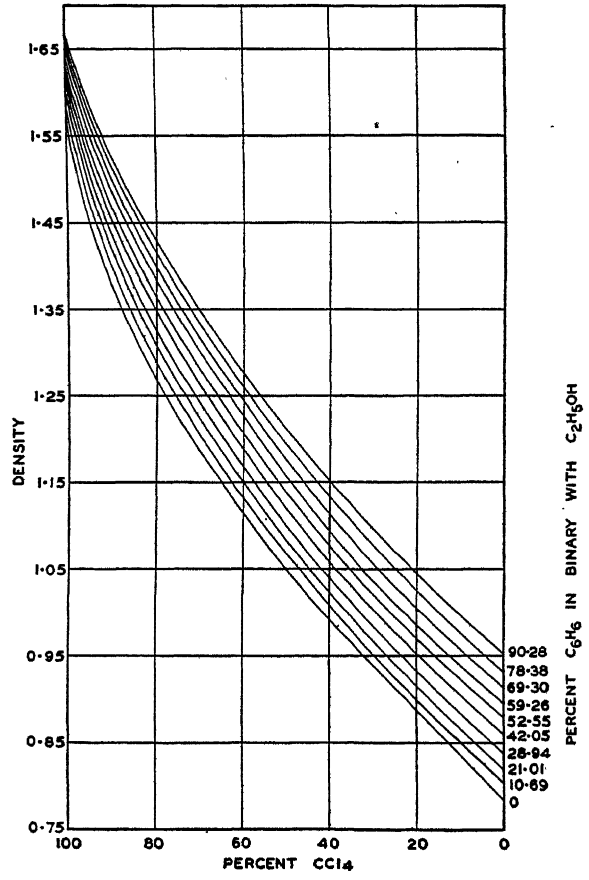

FIG. 5. *Experimental curves*—d_4^{25}.

DEVIATIONS FROM IDEALITY

Experimental curves (Figs. 4 to 7) throw no light on this question, but the maximum on Schreinemakers' vapour surface (19, 20) implies departure from ideality in most of these pseudobinary mixtures. From the results of our work it is possible to calculate approximate changes in specific volume and refractivity on mixing the components. Such calculations have already been made for the binary systems by Hubbard (7, 8), Barbaudy (1), and Hildebrand (6, Chap. V), to mention only a few. Figures for partial vapour pressures and temperature changes on mixing are at least equally important in a discussion

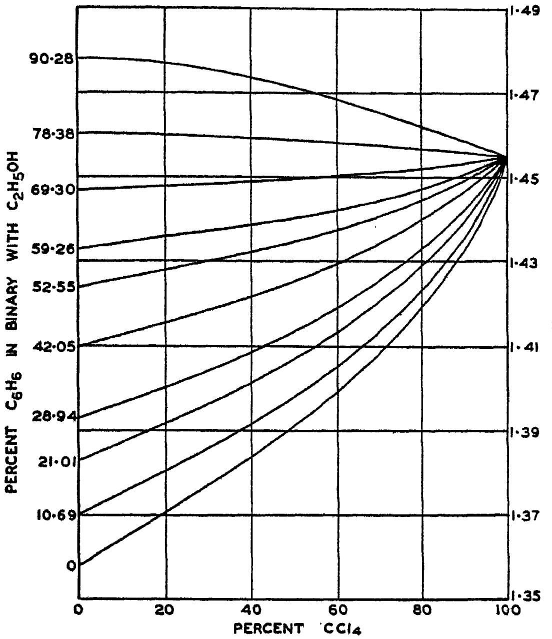

FIG. 6. *Experimental curves—N_D^{25}.*

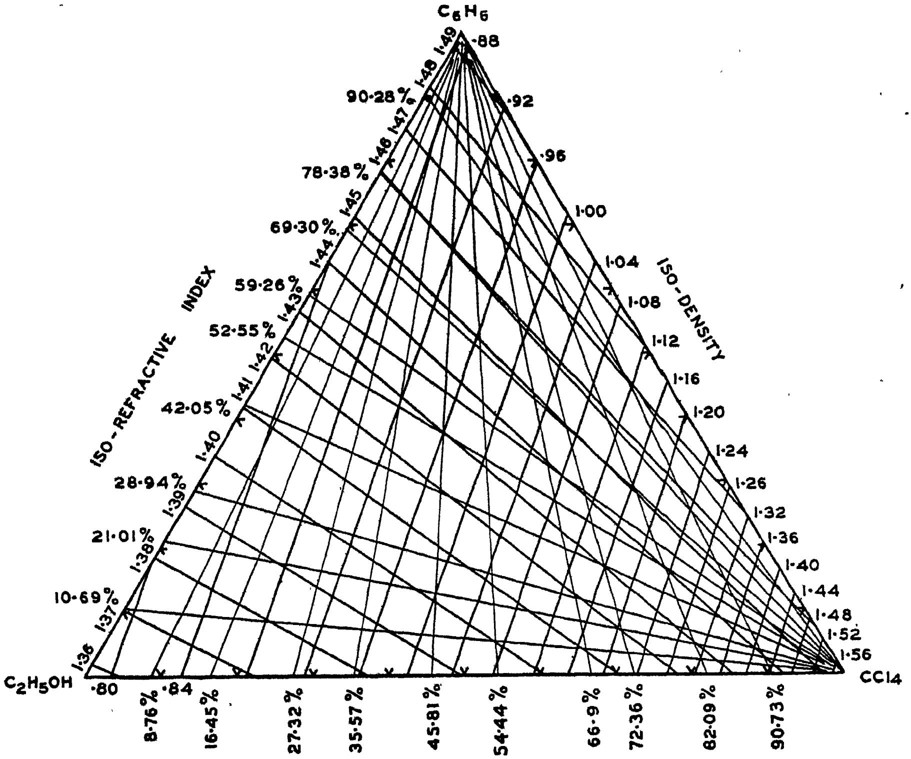

FIG. 7. *Analysis diagram for the system benzene – ethyl alcohol – carbon tetrachloride.*

of non-ideality. Therefore, though we have made calculations of molar volume and specific refractivity for all our systems, we do not reproduce the calculations, since the results are necessarily inconclusive. As far as can be judged on the imperfect basis of our experimental results, the departure from ideality is negligible for all systems except the alcohol – carbon tetrachloride binary, where the departure is still not great. The lack of ternary data on both partial pressures and temperature changes on mixing, however, rule out definite conclusions. Work now in progress will supply the partial pressure data when a more definite conclusion can be reached. Obviously, since most of these pseudobinary mixtures exhibit a maximum on the vapour pressure curve, the solutions cannot be ideal.

Partial molar volumes could be derived in various ways (Lewis and Randall (12)) from our data but they would merely represent a variation of the preceding discussion.

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THE CHROMATES OF SILVER AND COPPER[1]

By A. N. Campbell[2] and H. P. Lemaire[3]

Abstract

At 30° C. silver oxide reacts with an aqueous solution of chromium trioxide to form the normal silver chromate, Ag_2CrO_4, and a limited series of solid solutions of silver chromate in silver dichromate ($Ag_2Cr_2O_7$). The range of solid solubility is approximately 2% in terms of chromium trioxide, and extends from pure silver dichromate towards silver chromate. Both chromates of silver are sparingly soluble in water. No other chromates of silver were found to exist as solid phases at this temperature.

An examination of the system copper oxide – chromium trioxide – water shows that four chromates of copper can form at 30° C. They are: (i) copper dichromate, $CuCr_2O_7 . 2H_2O$, (ii) anhydrous normal copper chromate, $CuCrO_4$, (iii) a simple basic chromate, $CuCrO_4 . Cu(OH)_2$, and (iv) a 2 : 3 basic chromate, $2CuCrO_4 . 3Cu(OH)_2 . H_2O$. These chromates separate from solution in the above order as the chromate concentration is decreased, chromium trioxide itself being the initial solid phase. All four chromates are decomposed (partially) by water.

The solubility curves and ranges of existence have been established in most cases. Copper dichromate has a narrow range of existence, the normal chromate a relatively wide one. In part of this range, however, the chromate is in a metastable state, since it is in equilibrium with solutions that are supersaturated with respect to the simple basic chromate.

Introduction

With a view to establishing the existence and formulae of all the chromates of silver and of copper, systematic study was made of the systems: (i) silver oxide – chromium trioxide – water and (ii) copper oxide – chromium trioxide – water, at 30° C.

In 1906, Schreinemakers (9-13), in a series of papers, described his work on the chromates of the Group 1(*a*) metals. His method of investigation, carried out at 30° C., was the now well-known 'wet residue' method.

A search of the literature revealed that very little work had been done on the chromates of the Group 1 (*b*) metals, possibly because the chromates of the heavy metals are relatively insoluble and correspondingly more difficult to work with. The systematic investigation of the system silver oxide – chromium trioxide – water had never been undertaken. The system copper oxide – chromium trioxide – water had, however, been partially examined by Hayek (6) in 1934. His method was that of conductimetric measurements, not the solubility method, and his investigation was restricted to the basic region.

The object of this work was to complete the study of the Group 1 chromates by investigating those of silver, copper, and gold. Lack of time restricted the investigation to silver and copper, but, in any case, it is doubtful whether gold forms a chromate.

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Contribution from the Department of Chemistry, University of Manitoba, Winnipeg, Man.

[2] *Professor of Chemistry and Head of Department.*

[3] *Holder of a Bursary under the National Research Council of Canada, 1945–46.*

The Group 1(*a*) metals, according to Schreinemakers (9), form the following chromates, stable as solid phases at 30° C.

TABLE I

CHROMATES OF THE ALKALI METALS

Lithium	Sodium	Potassium	Rubidium	Caesium
$Li_2CrO_4 . 2H_2O$	Na_2CrO_4	K_2CrO_4	Rb_2CrO_4	Cs_2CrO_4
$Li_2Cr_2O_7 . 2H_2O$	$Na_4CrO_5 . 13H_2O$	$K_2Cr_2O_7$	$Rb_2Cr_2O_7$	$Cs_2Cr_2O_7$
	$Na_2CrO_4 . 4H_2O$	$K_2Cr_3O_{10}$	$Rb_2Cr_3O_{10}$	$Cs_3Cr_3O_{10}$
	$Na_2Cr_2O_7 . 2H_2O$	$K_2Cr_4O_{13}$	$Rb_2Cr_4O_{13}$	$Cs_2Cr_4O_{13}$
	$Na_2Cr_3O_{10} . H_2O$			
	$Na_2Cr_4O_{13} . 4H_2O$			

All the chromates of sodium and lithium, except the normal chromate of sodium, are hydrated, while none of the chromates of potassium, rubidium, or caesium contain water of crystallization. Only the lower chromates of potassium, rubidium, and caesium are stable in pure water; the tri- and tetrachromates decompose (partially) into lower chromates on entering solution. All these chromates are quite soluble in water.

The present investigation has shown that the analogy between the chromates of Group 1(*a*) and those of Group 1(*b*) is not close. Silver forms two chromates both of which are sparingly soluble in water at 30° C., while copper forms several chromates all of which are more soluble than those of silver, but not nearly as soluble as those of the Group 1 (*a*) metals. All the copper chromates are hydrated except the normal salt. In this respect the copper chromates resemble the sodium chromates, but no copper chromates above the dichromate were found. Another point of difference is that all the chromates of copper are unstable with respect to pure water.

The System: Silver Oxide - Chromium Trioxide - Water

Only the normal chromate and the dichromate of silver are known. Silver chromate can be prepared in various ways. Most of these involve the use of potassium chromate and a soluble salt of silver, usually the nitrate. It can also be prepared by the action of potassium chromate on silver oxide (4). Silver dichromate is prepared in much the same way, but with less difficulty. According to Moser (8), the action of chromic acid on a solution of silver nitrate furnishes crystals of silver dichromate, $Ag_2Cr_2O_7$. It can also be obtained by adding potassium dichromate to a solution of silver salt.

Silver chromate crystallizes in various colours, depending on the mode of preparation. There are two common forms; (*a*) the red-brown (varying from orange to deep reddish brown), and (*b*) the green (varying from dark green to greenish black, but red in transmitted light). It has now been proved (17) that the red and green silver chromates are identical in structure, the difference in colour being due to grain size only. In our work, only the red variety was obtained. The solubility at 30° C. is 2.9 mgm. per 100 gm. water (16).

Silver dichromate forms crystals that are dark brown or grey by reflected light and scarlet red by transmitted light (19). When boiled with water it forms the dark green chromate and an acid solution that deposits dichromate on cooling:

$$Ag_2Cr_2O_7 + H_2O = Ag_2CrO_4 + H_2CrO_4$$

Sherill (16) gives the solubility at 25° as 7.3×10^{-3} mole per litre.

EXPERIMENTAL

Preparation of Materials

Silver Oxide.—Silver oxide, Ag_2O, was prepared from silver nitrate and sodium hydroxide. A weak 5% sodium hydroxide solution was slowly added, in slight excess, to a 25% silver nitrate solution. The dark brown precipitate was washed several times with both hot and cold water and placed in a desiccator over water. Mellor (7, p. 372) states that silver oxide prepared in this way contains 1 or 2% silver hydroxide and probably traces of silver carbonate. Since silver oxide decomposes on drying, it was impossible to investigate the purity of the oxide by direct analysis. In any case, the presence of silver hydroxide would not alter the behaviour of the system.

Chromium Trioxide.—The chromium trioxide used was a British Drug Houses product of 99.87% purity.

Water.—The water was twice distilled and had a conductivity not greater than 10^{-5} mhos.

Methods of Analysis

The standard potassium thiocyanate method (Volhard's method) was employed to determine silver. The presence of chromate ion, however, presented a difficulty in determining the end-point. The usual end-point is obscured by the orange colour of the chromate ion and this difficulty increases with increasing concentration of chromate. It was therefore necessary to reduce the chromate ion to chromic ion by adding a small amount of sodium stannite. The colour was thereby changed from its original orange to a greenish-blue. The colour change at the end-point was then from blue to brown. The end-point was clearly indicated by a sudden darkening of the solution when one drop of potassium thiocyanate was added in excess. The accuracy of the method was checked by adding potassium dichromate solution to a solution of known silver content and then adding sodium stannite till the colour of the solution turned to a light blue. The solution was then analysed by the method described above, whereupon the analytical determination agreed with the known amount of silver.

Determination of chromate ion was carried out by the standard method of reducing the chromate with ferrous salt (15). The sample for analysis was dissolved in dilute sulphuric acid, not hydrochloric acid, so that the back titration could be performed with potassium permanganate instead of potassium dichromate.

Apparatus and Experimental Procedure

The thermostat operated at a temperature of 29.92° ± 0.03° C. The initial quantities of material were in each case 100 cc. water and 10 gm. wet silver oxide. Increasing quantities of chromium trioxide were added in successive trials to the above quantities of water and silver oxide.

To ensure attainment of equilibrium, conductimetric measurements were made daily on the mixtures, which were stirred constantly. These measurements also provided a measure of the rate of attainment of equilibrium. It

TABLE II

SOLUBILITY DATA IN THE SYSTEM $Ag_2O - CrO_3 - H_2O$ AT 29.9° C.

Sample No.	Wt. CrO_3	Time of stirring, days	Nature of solid phase	Specific conductivity, mhos	Analysis, % liquid phase and wet solid phase, respectively			
					Liquid phase		Wet solid phase	
					Ag_2O	CrO_3	Ag_2O	CrO_3
1	0.5 gm	3	Silver oxide and silver chromate	1.76×10^{-4}	Trace	—	55.2	4.01
2	1.0	3	" "	1.69×10^{-4}	Trace	—	52.4	8.93
3	1.5	3	" "	2.09×10^{-4}	Trace	—	30.2	6.76
4	2.0	3	" "	4.13×10^{-4}	Trace	—	51.2	15.3
5	2.5	3	" "	8.28×10^{-4}	Trace	—	51.9	18.9
6	3.0	4	Silver chromate and solid solution	5.82×10^{-3}	0.09	0.21	50.6	25.1
7	3.5	5	" "	5.93×10^{-3}	0.08	0.21	52.9	26.5
8	4.0	4	" "	5.20×10^{-3}	0.11	0.19	49.9	29.4
9	5.0	6	" "	5.01×10^{-3}	0.10	0.18	45.6	34.1
10	6.0	8	Solid solution	1.11×10^{-2}	0.07	0.34	44.7	35.5
11	8.0	—	" "	3.81×10^{-2}	0.08	2.55	44.3	35.7
12	10	5	" "	6.04×10^{-2}	0.1	4.07	43.4	35.8
13	14	21	" "	9.32×10^{-2}	0.1	7.11	46.2	38.6
14	15	6	" "	8.56×10^{-2}	0.1	8.11	44.3	38.1
15	25	8	" "	1.07×10^{-1}	0.1	15.4	40.7 40.8	38.4 37.7
16	40	8	" "	1.00×10^{-1}	0.1	24.0 23.9	38.4 38.7	39.1 39.4
17	70	6	" "	—	0.1	35.1	42.4 37.5	43.4 42.4
18	100	8	" "	—	0.1	46.9 47.0	40.9 38.1	46.1 46.0
19	130	8	" "	—	0.1	53.5 53.6	40.4 37.8	47.7 48.2
20	170	8	" "	—	0.1	58.5 58.9	39.8 36.0	49.5 50.3
21	190	8	Silver dichromate and CrO_3	—	0.1	61.9 62.0	31.3 29.4	57.0 57.3
22	200	8	Silver dichromate and CrO_3	—	0.1	61.9 61.9	23.5 24.9	64.3 64.6

will be shown in the discussion of results that the conductimetric method is not always sensitive enough, and then a false equilibrium, slightly removed from the true equilibrium, sometimes results.

The resistance of samples of low conductivity was considerably affected by gaseous impurities derived from the air of the laboratory. To compensate for this error, a blank containing distilled water only was kept in the thermostat with the sample under investigation. The conductivity of the blank was subtracted from the conductivity of the test sample. Solutions containing more than 40 gm. of chromium trioxide per 100 gm. of water had a very high conductivity and it was impossible to make resistance measurements of any useful accuracy on these samples.

The filtration apparatus was of the standard type. It included a ground glass filter with a tube connecting it to the filtrate bottle which, in turn, was attached to the filter pump. The analyses were frequently made in duplicate.

Results

Table II contains the analyses of liquid phases and equilibrium wet solid phases, as well as the conductivity data. The equilibrium data are plotted in Fig. 1 in weight per cent.

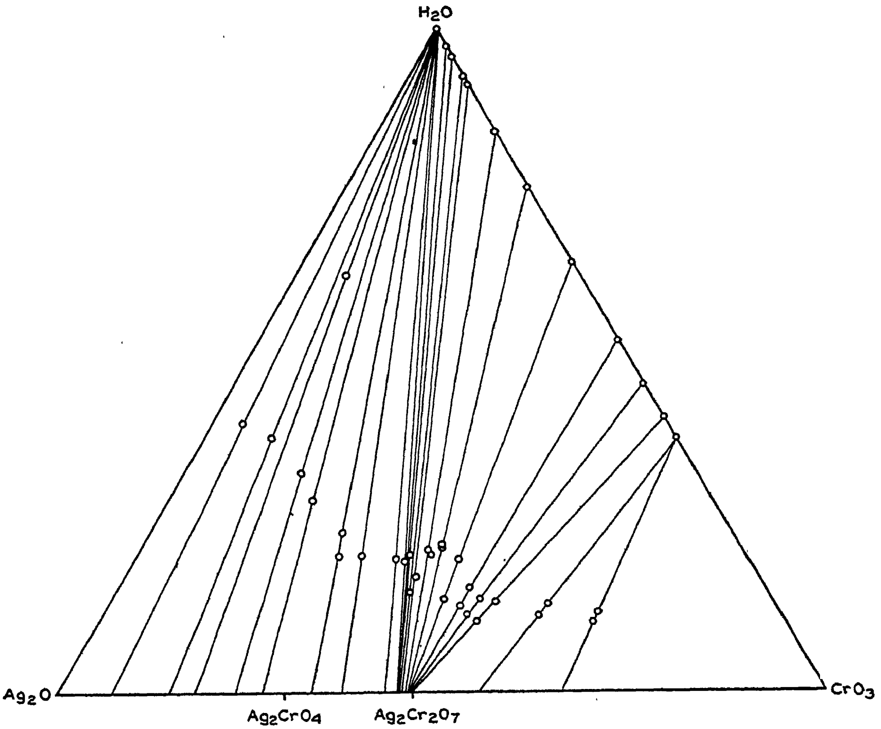

FIG. 1.

DISCUSSION OF RESULTS

Because of the very low solubility of silver oxide and the chromates of silver, Fig. 1 gives no information as to the formation of normal silver chromate at 30° C., but its existence is clearly shown in Figs. 2 and 3. In Fig. 2 the initial quantity of chromium trioxide in the sample is plotted as abscissa and the percentage of chromium trioxide in solution as ordinate. In Fig. 3 the total amount of chromium trioxide is again plotted as abscissa, and the conductivity of solution as ordinate.

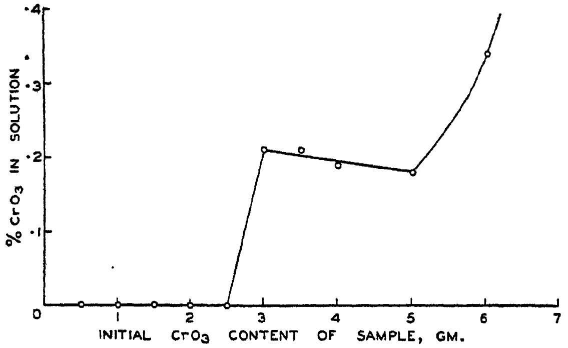

FIG. 2.

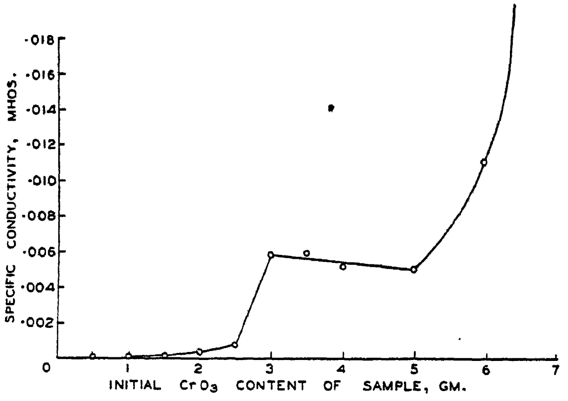

FIG. 3.

In a system of three components, two solid phases in equilibrium with solution constitute an isothermally invariant system. The composition of the solution therefore remains constant until one or other of the solid phases disappears.

The wet silver oxide employed in this work contained 65.4% silver oxide. The amount of chromium trioxide necessary to convert completely 10 gm. of the wet oxide to silver chromate, Ag_2CrO_4, is therefore 2.8 gm. Figs. 2 and 3 indicate that samples containing 0.5 to 2.5 gm. chromium trioxide give rise to a liquid phase of constant composition and the same is true of samples containing 3.0 to 5.0 gm. chromium trioxide. In the 2.5 to 3.0 gm. range both the chromium trioxide in solution and the conductivity jump suddenly to a higher constant value. This indicates that in this range one solid phase, the oxide, disappears and the system gains one degree of freedom.

The first heterogeneous solid mixture is therefore composed of silver oxide and silver chromate. When enough chromium trioxide has been added to convert all the oxide to the chromate (2.8 gm.) the system becomes for a short range of concentration isothermally univariant, i.e., the composition of the saturated solution changes, but it soon attains a second constant value because a new compound appears, making the solid system once more heterogeneous, i.e., it is now a mixture of silver chromate and of saturated solid solution of silver chromate in silver dichromate. The limit of solid solubility is indicated in Figs. 2 and 3 by a break in the curve when the total chromium trioxide content of the sample is 5 gm. After this point the system is isothermally univariant and the curve rises very rapidly as chromium trioxide builds up in solution.

The range of solid solution as determined from Fig. 1, is about 2% chromium trioxide, one limit being pure dichromate and the other solid solution of chromate in dichromate: it is impossible to say, because of the low solubility of silver chromate, whether there is a corresponding solid solubility of dichromate in chromate; the conductivity method is not sufficiently sensitive to answer the question either.

The departure from ideal behaviour in Figs. 2 and 3, e.g., 'horizontals' not truly horizontal, is due to the fact that in these sparingly soluble systems equilibrium is approached very slowly. The conductivity is at first high when the chromium trioxide is added and then falls off asymptotically with time, as the dissolved chromium trioxide is converted to 'insoluble' chromate. It is thus very natural that solutions were sometimes taken to be equilibrium solutions which were not really so. The difference in the analytical results is, however, negligible.

The heterogeneous mixture of silver oxide and silver chromate was dark brown while the heterogeneous mixture of silver chromate and saturated solid solution was of a more reddish shade. Both mixtures appeared as blood red crystals in transmitted light under the microscope.

The System: Copper Oxide - Chromium Trioxide - Water

Four chromates of copper are described in the literature:— copper dichromate, normal copper chromate, and two basic copper chromates, the compositions of which are in doubt.

Copper dichromate crystals were first isolated by Droege (3) in 1857. He assigned to the compound the formula $CuCr_2O_7 . 2H_2O$. J. Schulze (14) and M. Gröger (5) also succeeded in isolating crystals of this composition by the action of chromium trioxide solution on copper carbonate. Gröger also claims the existence of anhydrous copper dichromate and of a compound $CuCr_4O_{13} . 2H_2O$. This is the only occasion on which a higher chromate than the dichromate is claimed to exist.

The copper dichromate crystals are described in the literature as blackish-brown in colour, but those obtained by us were usually a bright wine-red, but in the presence of a large amount of adhering mother liquor their colour seemed much darker.

All investigators, except one, claim that the normal chromate is anhydrous. Briggs (2) assigns to this salt the formula $CuCrO_4 . 2H_2O$, but our systematic investigation shows that the normal chromate is anhydrous.

There is, or has been, considerable controversy regarding the composition of the basic chromates of copper. Copper trioxychromate ($CuCrO_4 . 3Cu(OH)_2$) is said to be produced by the action of an excess of an alkaline solution of potassium chromate on a solution of copper sulphate, but according to Schulze (14) and Gröger (5), the chromate formed in this way is the dioxychromate ($CuCrO_4 . 2Cu(OH)_2$).

The only systematic investigation of the system copper oxide – chromium trioxide – water is that of Hayek (6) in 1934. His work, carried out at 40° C., showed the existence of two basic chromates, viz., $2CuCrO_4 . 3Cu(OH)_2 . H_2O$ and $CuCrO_4 . Cu(OH)_2$. Hayek's experimental procedure consisted in stirring various proportions of copper oxide and chromium trioxide in 100 cc. of water till constant conductivity was attained, i.e., essentially the same method as we used in the investigation of the silver chromates. The yellowish-brown 3 : 3 basic chromate formed even at the greatest dilutions. This salt corresponds to the dioxychromate, $CuCrO_4 . 2Cu(OH)_2$, obtained by previous workers, and Hayek believes that the greater proportion of base in the dioxychromate results from the decomposition by boiling of the 3 : 2 basic salt, which is not stable in hot water.

The simple basic salt, $CuCrO_4 . Cu(OH)_2$, occurs in two forms—a copper red and a chocolate brown to lilac form. This is probably the brownish precipitate mentioned by Gröger (5), which deposits previous to the formation of the lower chromate. Hayek found that boiling the simple basic chromate with water results in the formation of a yellow salt, but he does not attribute the change in colour to a change in composition but to a change in superficial colouring, the brown appearance being caused by a superficial layer of chromic acid and the yellow colour by a layer of hydroxyl ions or $Cu(OH)_2$ molecules.

Although our investigation is restricted mostly to the acid region, the few experiments conducted in the basic region have yielded results in conformity with those of Hayek.

EXPERIMENTAL

Preparation of Copper Oxide

The method by which the copper oxide was prepared was found to have considerable influence on the progress of the work. The copper oxide of commerce, which has no doubt been ignited, fails to react to any appreciable extent with chromium trioxide. Our attempts to prepare pure copper oxide by the action of sodium hydroxide on copper sulphate failed, because it is very difficult to remove all the sulphate from the copper oxide by washing. We finally succeeded by using the method of Vogel and Reischauer (18). According to this method, a neutral solution of copper nitrate is divided into two equal parts. To one half, concentrated ammonia is added until the precipitated copper hydroxide redissolves. This portion is then added slowly to the other half and the mixture boiled under reflux for four hours; the copper hydroxide which forms at first is thus converted to copper oxide. The oxide is filtered hot and washed twice with hot water and once with cold. To remove the final traces of nitrate, the copper oxide is boiled under reflux for another three hours, and again washed several times with hot and cold water till the oxide is free from nitrate.

Method of Analysis

Chromate was determined as described under the chromates of silver. Copper was determined electrolytically. For solutions containing high chromate concentrations, the copper was checked gravimetrically as cuprous sulphide. The high concentration of chromate was found not to interfere with the electrolytic determination.

RESULTS

The analytical results are contained in Table III, and are plotted in Fig. 4, in weight per cent.

DISCUSSION OF RESULTS

Time of stirring was the most important factor in this work. Depending on the nature of the solid phase, some samples took only a short time to attain equilibrium while others were extremely sluggish in their behaviour. In samples in which chromium trioxide was the solid phase, equilibrium was established relatively quickly in two or three days. With copper dichromate as solid phase, two weeks were necessary, while with copper chromate a month was required. When the stirring was not carried on for a sufficient length of time, the action on the copper oxide was incomplete. In general, the time required to attain equilibrium increased with decreasing chromate concentration in solution.

Five different solid phases may be in equilibrium with solution, depending on the chromate concentration, viz.:— (i) chromium trioxide, CrO_3 ; (ii) copper dichromate, $CuCr_2O_7 . 2H_2O$; (iii) anhydrous normal copper chromate, $CuCrO_4$; (iv) simple basic chromate, $CuCrO_4 . Cu(OH)_2$; (v) 2 : 3 basic chromate, $2\ CuCrO_4 . 3Cu(OH)_2 . H_2O$.

Straight lines joining the composition of the solid phases to the apex of the triangle of the equilibrium diagram do not intersect the respective solubility curves. All four chromates, therefore, decompose partially (are incongruently soluble) when brought into contact with pure water.

TABLE III

SOLUBILITY DATA IN THE SYSTEM $CuO - CrO_3 - H_2O$ AT 29.9° C.

Sample No.	Time of stirring	Nature of solid phase	Analysis, % liquid phase and wet solid phase, respectively			
			Liquid phase		Wet solid phase	
			CuO	CrO_3	CuO	CrO_3
1	2 days	CrO_3	—	64.8	—	100
2	3 "	"	1.0	64.4	Trace	97.4
3	3 "	"	5.7	62.1	0.9	95.0
4	3 "	"	10.9	60.6	1.11	96.3
5	3 "	"	12.6	61.0	2.76	93.8
6	2 weeks	$CuCr_2O_7 . 2H_2O$ and CrO_3	13.2	61.8	19.7	64.9
7	2 "	" "	13.1	61.7	14.5	72.4
					20.3	62.6
8	2 "	$CuCr_2O_7 . 2H_2O$	13.8	60.7	20.8	62.8
9	2 "	"	14.6	58.6	20.4	61.0
					22.0	60.4
10	2 "	"	15.0	54.7	22.0	60.4
11	4 "	$CuCrO_4$	14.5	53.1	28.2	54.0
12	4 "	"	15.1	47.4	28.7	51.1
					26.1	50.0
13	4 "	"	15.4	46.9	27.6	50.1
14	4 "	"	15.0	40.5	26.3	45.8
15	2 "	"	12.7	31.9	25.1	41.0
					23.7	37.5
16	2 "	"	10.1	25.4	21.1	34.7
17	2 "	"	8.80	22.3	23.1	35.9
18	1 "	"	7.94	19.6	29.3	40.4
19	1 "	"	6.60	16.6	27.6	38.0
20	1 "	"	5.80	14.8	21.6	30.4
21	1 "	"	4.31	11.3	29.0	38.6
					22.9	30.8
22	5 days	$CuCrO_4 . Cu(OH)_2$	6.80	10.5	23.0	31.2
23	5 "	"	5.70	8.53	35.6	24.8
24	5 "	$2CuCrO_4 . 3Cu(OH)_2 . H_2O$	4.74	7.31	31.0	18.2
			4.74	7.32	30.7	17.9
25	5 "	"	2.40	5.88	31.7	18.6
			2.42	5.89	30.3	18.3

Only a few experiments were made in the region of basic salt. The few results obtained are in accordance with the findings of Hayek (6), viz., simple basic chromate, $CuCrO_4 . Cu(OH)_2$, and 2 : 3 basic chromate, $2CuCrO_4 . 3Cu(OH)_2 . H_2O$. Both the basic chromates are yellow, the normal chromate forms dark-yellow crystals in the dilute region and brownish-red ones in the more concentrated region, while the dichromate crystallizes in bright red-wine needles.

Only one invariant point was established experimentally, viz., the chromium trioxide – copper dichromate invariant. The invariant for which the solid phases are normal chromate and dichromate should be realizable but it was not established in this investigation. It has been narrowed down, however, to a very small range of concentration. The solubilities of the basic chromates are so small that the intersection of their respective solubility curves at invariance is not detectable.

The solubility curves of the simple basic chromate and the normal chromate do not intersect. For some undetermined region of concentration, therefore, the normal copper chromate must be in a metastable state. The reason for lack of definiteness in the data here is the very great slowness with which true equilibrium is attained in the solutions containing less chromate.

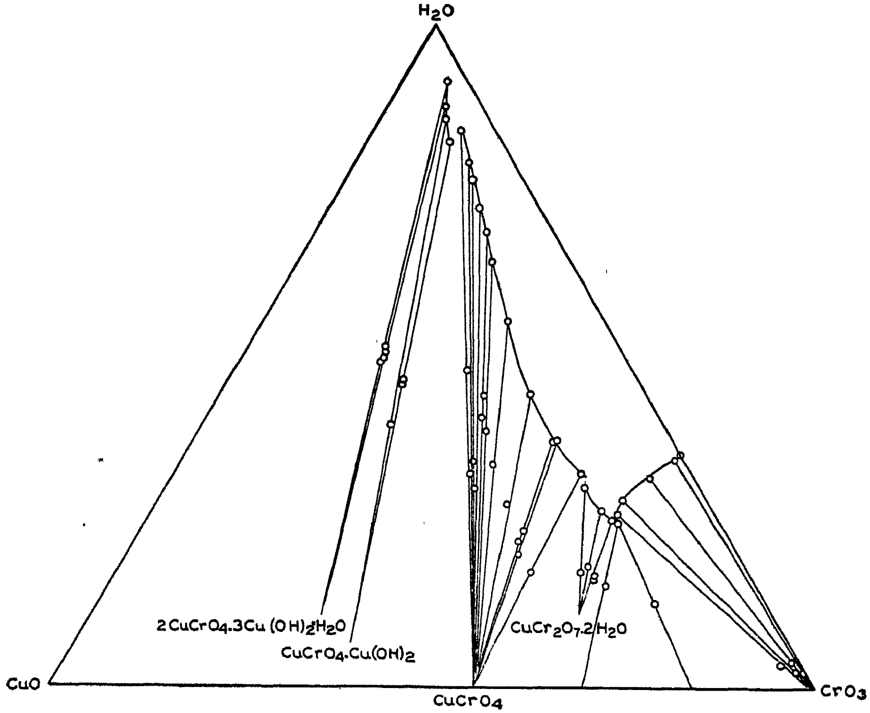

FIG. 4.

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THE DETERMINATION OF PARTICLE SIZE BY LIGHT SCATTERING[1]

By J. Bardwell[2] and C. Sivertz[3]

Abstract

A critical study has been made of the various observations necessary for the determination of the size of small dielectric particles by the Debye–Einstein equation, which can take the form:

$$\text{Mass of particle} = \frac{3}{32\pi^3}\frac{\lambda^4}{\mu_0^2}\left(\frac{d\tau}{dc}\right)_{c=0} \Bigg/ \left(\frac{d\mu}{dc}\right)^2 .$$

The turbidity measurements were made with a Beckman spectrophotometer and those of refractive index with a Zeiss dipping refractometer. This article deals especially with the determination of the turbidity and refractive index gradients. The method was applied to the determination of latex particle size and gave results in good agreement with independent methods.

Introduction

Methods for the determination of the size of particles of colloidal dimensions have in recent years become of increasing importance. Much of this new interest has arisen from the wide field of observation opened up by the development of the ultracentrifuge and the electron microscope. However, the application of these techniques is greatly limited by their availability, and to some extent by the conditions of observation that must be met. Consequently, a relatively simple technique for particle size determination involving light-scattering measurements may be expected to find wide application and interest. It is the object of this paper to present a detailed account of the application of such a technique based upon the theoretical work of Einstein (2) and Debye (1), in the belief that this technique constitutes a powerful tool in the hands of research workers.

For example, during the preparation of this paper on the particle size of synthetic latex, G. Oster (5) described a similar method for the determination of the molecular weight of certain viruses.

While the method described below is a very welcome addition to the relatively few absolute methods of size determination, it has certain limitations, chief of which is its restriction to sizes that are small relative to the wavelength of the light scattered. Nevertheless, there remains a large region of particle sizes to which the method may be applied.

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[2] *Graduate student.*

[3] *Associate Professor of Chemistry.*

Theoretical

Debye's (1) modification of Einstein's equation for critical opalescence results in the following expression for the turbidity of solutions:

$$\tau = \frac{8\pi^3}{3}\frac{kT}{\lambda^4}\frac{\left(c\frac{d\epsilon}{dc}\right)^2}{c\left(\frac{dP}{dc}\right)}, \tag{1}$$

where the turbidity, $\tau = 2.303\ D$, and D is the optical density of a solution of unit length.

ϵ = optical dielectric constant = μ^2 for non-absorbing systems,

μ = the refractive index at wave-length λ,

P = osmotic pressure,

c = number of grams per cubic centimetre of solute.

An analysis of the variables in Equation (1) reveals that τ, c, μ, T, and λ are all capable of direct measurement and consequently it is the *osmotic pressure gradient that this equation does in fact evaluate.* Now, osmotic pressure may be adequately expressed by an equation of the form

$$P = kT\left[\frac{c}{m} + A_2c^2 + A_3c^3 + \ldots\right], \tag{2}$$

where A_2 is the second virial coefficient and m is the mass of the particle. Introducing the value of the derivative $\frac{dP}{dc}$ from Equation (2) in Equation (1) (neglecting higher than squared terms), and the differential $d\epsilon$ as $2\mu\ d\mu$, yields,

$$\tau = \frac{32\pi^3}{3\lambda^4}\cdot\frac{\mu_0^2\left(\frac{d\mu}{dc}\right)^2 c\cdot m}{\{1 + 2\ A_2mc\}}. \tag{3}$$

Since the refractive index, μ, of the entire sol at low concentration differs only slightly from μ_0, the refractive index of the medium, the latter is conveniently used in place of the former in Equation (3).

Now the mass of the particle m that is implicit in Equation (3) may be expressed either as a function of τ/c; i.e.

$$m = \frac{3\lambda^4}{32\pi^3}\frac{\tau/c\ (1 + 2\ A_2mc)}{\mu_0^2\left(\frac{d\mu}{dc}\right)^2}, \tag{4}$$

or in terms of the specific turbidity $\left(\frac{d\tau}{dc}\right)$ obtained by differentiating Equation (3), i.e.,

$$\frac{3\lambda^4}{32\pi^3}\frac{\left(\frac{d\tau}{dc}\right)(1 + 2\ A_2mc)^2}{\mu_0^2\left(\frac{d\mu}{dc}\right)^2}. \tag{5}$$

Equations (4) and (5) are true for all values of c for which the osmotic pressure equation holds. They are of interest to show how deviations from the Van't Hoff equation for osmotic pressure might be expected to influence the determination of particle mass. In practice the observed values of τ/c are extrapolated to $c \doteq 0$, where of necessity $\lim_{c=0} \frac{\tau}{c} = \lim_{c=0} \frac{d\tau}{dc}$.

Equations (4) and (5) form the basis of calculations of m and A_2 from experimental measurements of concentration, turbidity, and refractive index at a definite wave-length.

Experimental

(a) MEASUREMENT OF TURBIDITY

Measurements of turbidity have been widely used (6) in quantitative analysis to estimate the concentration of dispersed material, on the assumption of similar particle size. Equation (3) indicates that size can be *evaluated* by measurement of both concentration and turbidity at a known wave-length.

Implicit in the above theory is the assumption of symmetrical distribution of the scattered radiation. This exists provided the particle diameter, d, is small compared to the wave-length. ($d = \frac{\lambda}{20}$ or less.) For particles of diameter comparable to the wave-length, phase differences result in dissymmetry in the scattered radiation with more forward than backward scattering (Mie effect) (4). Consequently when $d > \lambda/20$ the calculated values of size are smaller than the true values. However, a correction can be applied, which amounts to less than 5% for the sizes studied in this case, namely, up to 1000 Å.

The Beckman spectrophotometer was chosen for light-scattering measurements since it readily provides a precise and absolute value of the turbidity as defined above. The monochromator provides an accurately calibrated beam of essentially monochromatic light (band width 5 to 20 Å) over a large range of the spectrum (2200 to 10,000 Å) and so the instrument is also suitable for the measurement of wave-length exponent. In the transmittance region of 6 to 97% the precision is 0.1 to 0.5%.

Since measurements of apparent absorption are substituted for measurements of scattering it is important that the 'consumptive' absorption of the dispersed material be negligible compared to the 'conservative' absorption. That this condition is fulfilled in the case of latex is indicated by the close adherence for all wave-lengths to the inverse nth power of wave-length in the measured turbidity (Fig. 1). Even if this were not the case, a wave-length could be found to minimize the effect of consumptive absorption. This flexibility is one of the advantages of the use of such a spectrophotometer.

Fig. 1 shows the results of measurements, in the region 3200 to 10,000 Å, of the turbidity of a series of concentrations of GR-S latex. The average particle diameter of this latex was 940 Å. A study of Fig. 1 reveals the following characteristics.

(1) Linearity of log D vs. log λ over a large range of wave-length for all concentrations. The slopes of the linear regions are found to lie close to the average value of 3.45.

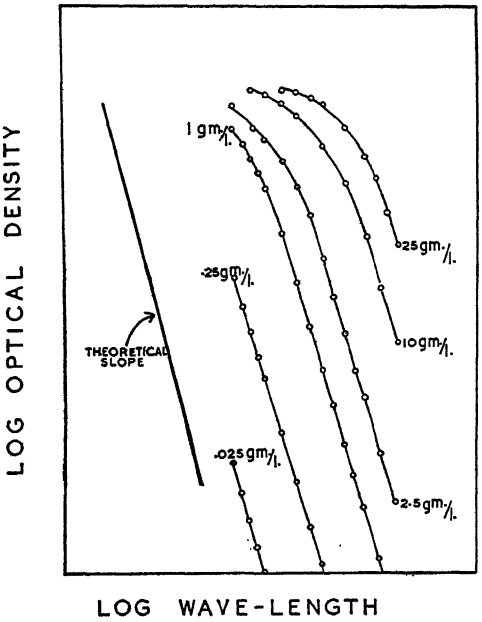

FIG. 1. *The turbidity of solutions of small dielectric particles (latex) as a function of wave-length.*

(2) Above an optical density of 1.2 there is a marked decrease in the value of the wave-length exponent (slope) for all concentrations. This is believed to be due to the effect of diffusion of light caused by secondary scattering.

If Equation (1) is generalized to $\tau = A\,\lambda^n$ we find at least three reasons for deviation of $-n$ as measured, from the theoretical value of 4. The effect of secondary scattering is a decrease in the value of $-n$ from the theoretical. The dispersion of refractive index with wave-length as approximated by the Cauchy equation,

$$\mu = a + \frac{b}{\lambda^2},$$

predicts a value of $-n > 4$.

The major reason for the observed value of $-n = 3.45$ is, however, the fact that the particles are somewhat too large for symmetrical scattering except at the longest wave-lengths used. Similar measurements with particles of diameter 1500 Å gave a value of $-n = 2.5$. This suggests another method of particle size estimation in a certain range, namely, the variation of wave-length exponent. A study of this has recently been made by Dr. W. Heller (3).

When a satisfactory theory relating the wave-length exponent to particle size and shape is evolved, it should provide a convenient method for the determination of these latter properties. In the absence of such theory no extensive experimentation was carried out in this study.

In the case of a sol of unknown particle size it is desirable to have qualitative knowledge of the ratio of d/λ. This may readily be obtained by measurement of the wave-length exponent. In our experience, for wave-length exponent values higher than three, the method is subject to no serious error.

Constant wave-length sections of the family of curves in Fig. 1 are shown in Fig. 2. Deviations from linearity are noted in all cases, especially at the larger values of both turbidity and concentration. These effects result from secondary scattering and the deviations from ideal osmotic behaviour described in Equation (2).

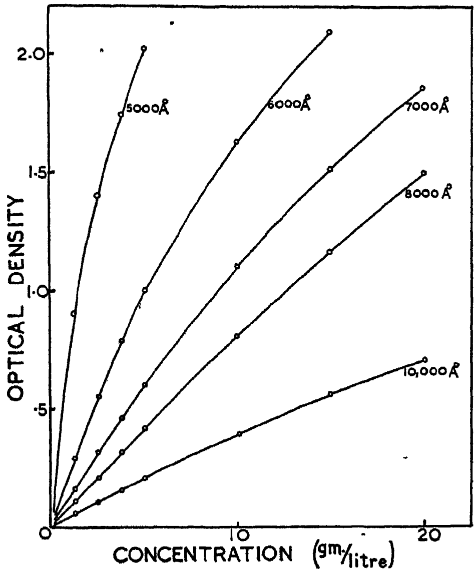

Fig. 2. *Turbidity as a function of concentration.*

Two methods have been employed in this work to obviate the complexities referred to in the preceding paragraphs.

First Method: Use of a Combination of Wave-lengths

Equation (4) may be written as follows for the region $c \doteqdot 0$,

$$M = \frac{4.22 \times 10^{21}}{\mu_0^2 \left(\dfrac{d\mu}{dc}\right)^2} \cdot \frac{D\,\lambda^4}{c}\,, \qquad (6)$$

where M is the mole weight of the light scattering material, i.e., Avogadro's number times the m of Equation (4). It is worth noting that a simultaneous knowledge of M, the mole weight of the latex particle, and $\bar{M}$, the average molecular weight of the *polymer molecule* of which the former is composed, will at once reveal the number of average polymer molecules contained in an average latex particle. This amounts to about 1000 molecules per latex particle for the largest particles found in this study.

Since for small particles the wave-length exponent approaches 4, the value of $D\,\lambda^4$ may be obtained as the slope of the D vs. λ^{-4} plot as shown in Fig. 3. Extrapolation of the derived values of $\frac{D\,\lambda^4}{c}$ to zero concentration eliminates the effect of both secondary scattering and the higher terms in Equation (2).

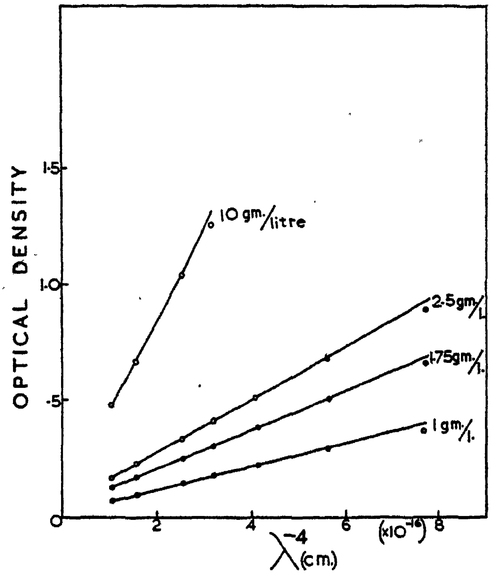

FIG. 3. *Turbidity as a function of inverse fourth power of wave-length.*

The only measurements now remaining for the calculation of M are those of μ_0 and $\frac{d\mu}{dc}$, which are further discussed below.

The equivalent of this method was recently reported in connection with the determination of the molecular weights of viruses (5). It is to be noted that this method requires dispersion corrections of μ_0 and $\frac{d\mu}{dc}$ (neglected in Reference (5)) to the appropriate wave-lengths, and since these involve some uncertainties the following method was chosen instead.

Second Method: Use of a Single Wave-length

Because the refractive index as measured by commercial refractometers is for $\lambda = 5893$ Å, this wave-length was chosen for scattering measurements. In general this allows use of concentrations of the same order of magnitude for both light scattering and refractive index. The refractive index μ_0 of the medium for the latex systems studied was found to be 1.33. Use of these numerical values of λ and μ, and expressing m as the mole weight, Equation (5), in the limit of zero concentration, becomes

$$M = 28450 \cdot \frac{\left(\frac{dD}{dc}\right)_0}{\left(\frac{d\mu}{dc}\right)^2}, \tag{5}$$

where $\frac{d\mu}{dc}$ = specific refractive index and $\left(\frac{dD}{dc}\right)_0$ = specific optical density obtained by extrapolation of measured values of $\frac{D}{c}$ to zero concentration or to zero turbidity. It was found convenient to prepare the required solutions by successive addition of aliquot portions of concentrated polymer solution to the solvent. (Fig. 4 indicates the extrapolation for a series of GR-S latices of increasing conversion.)

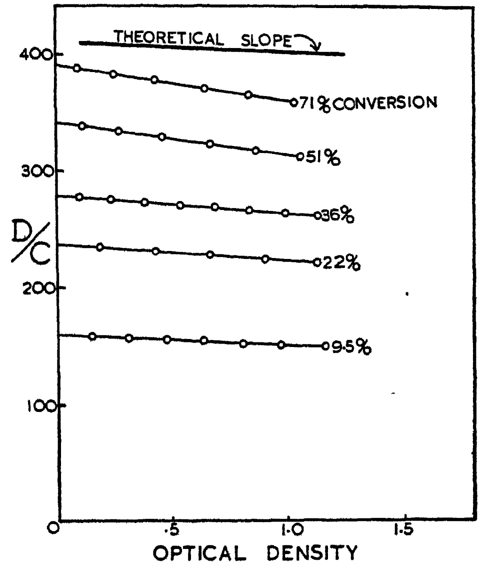

FIG. 4. *Extrapolation of the turbidity gradient to infinite dilution.*

(*b*) MEASUREMENT OF $\frac{d\mu}{dc}$, THE SPECIFIC REFRACTIVE INDEX

Measurement of the specific refractive index involves the determination of relatively small differences. Furthermore the turbidity of these sols restricts the use of commercial refractometers to quite low concentrations.

In spite of these difficulties use of the Zeiss dipping refractometer was found feasible. Consideration of the average deviation of instrumental readings and the temperature coefficient of refractive index indicated that temperature control of ± 0.1° C. was adequate for successive determinations of refractive indices of solvent and solution. By the use of the auxiliary prism, clear definition was obtainable up to a concentration of 15 gm. per litre.

The value of $\frac{d\mu}{dc}$ can be expected to be constant for all concentrations. This was verified by experiment (Fig. 5). The value of $\frac{d\mu}{dc}$ can thus be calculated from *one* measurement of the solvent and *one* of the polymer solution of suitable concentration. The resultant precision is 1 to 2%.

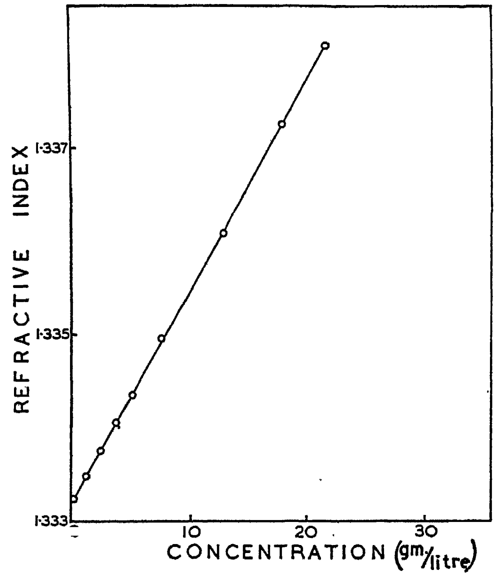

FIG. 5. *Refractive index of latex of different concentrations.*

It is worth noting that the value of $\frac{d\mu}{dc}$ may be *calculated* in certain cases, namely, when the refractive index of the suspended particle is known, and is independent of the composition of the medium. In this case $\frac{d\mu}{dc}$ is equal to the difference of refractive index of the suspended particle and of the medium divided by the density of the suspended phase. This is particularly useful when the sol to be investigated is very dilute.

Finally μ_0 is the refractive index of the liquid in which the particle is suspended. For example, in this work the medium is a 0.1% solution of soap.

(c) MEASUREMENT OF CONCENTRATION

The concentration in grams per cubic centimetre was calculated from a gravimetric determination of the material which is non-volatile at 60° C. in a vacuum oven.

Particle density was obtained by use of a pycnometer.

AGGLOMERATION ON DILUTION

The high turbidity of latex to visible radiation made dilutions of 10 to 100 volumes necessary. When water was used, an appreciable agglomeration took place, resulting in slow increases in specific turbidity with time. This instability was overcome by using as diluent a 0.1% soap solution. Such dilution might be avoided completely, if necessary, by the use of infra-red radiation or of thinner absorption cells.

APPLICATION OF METHOD TO GR-S LATEX

The technique described above was applied to the determination of the size of polymer particles present in a series of synthetic rubber latices. These latices represent different stages of conversion of monomers into rubber macromolecules.

In addition to the method of light scattering, an independent method was applied by Mr. J. Wright in this laboratory, based on the fact that the total surface of the dispersed phase of such an emulsion may be determined and hence an average particle size calculated.

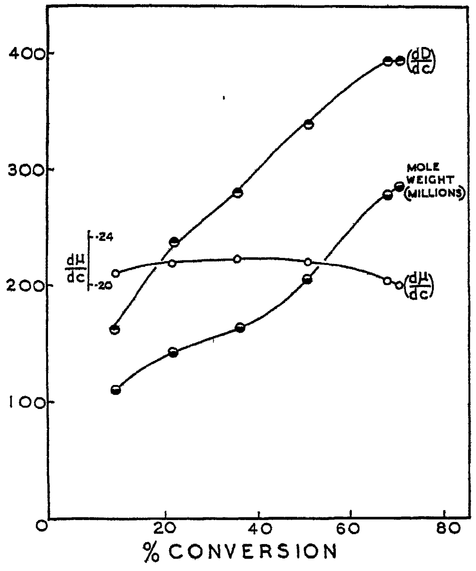

FIG. 6. *Changes of specific turbidity, specific refractive index, and particle size of latex during polymerization.*

Fig. 6 shows the values of specific refractive index, specific turbidity, and mole weight at different conversions as determined by means of the optical measurements. It is noted that the growth of size is almost entirely reflected by changes in the specific turbidity. The small variations of specific refractive index are due to changes in composition of the polymer particles.

In Fig. 7 is shown a comparison of mole weights determined by the light scattering and surface area methods.

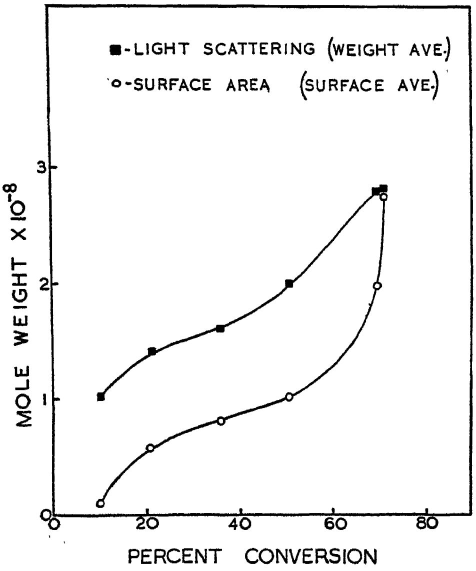

FIG. 7. *Comparison of particle size by light scattering and surface area methods.*

Discussion of Experimental Results

It is not the object of this paper to discuss the implications of these results in the synthesis of rubber, but rather to draw attention to a technique by which the size of particles of this nature may be evaluated.

In general, the results found for latex particles by this method agree with those found with the electron microscope.

The observed differences in size in Fig. 7 can be attributed to two factors. First, the light scattering method includes the total mass, whereas that of surface area does not include the emulsifier. Second, while light scattering gives a weight average particle weight, $\frac{\Sigma\, n_i\, m_i^2}{\Sigma\, n_i\, m_i}$, surface area gives a 'surface average',

$$\left[\frac{\Sigma\, n_i\, m_i}{\Sigma\, n_i\, m_i^{2/3}}\right]^3 .$$

Only in the case of perfect homogeneity will these 'averages' coincide. Consequently the observed differences might be translated into a measure of the heterogeneity of particle size.

The slopes of the lines in Fig. 4 are due in part to the deviations from ideality expressed by the coefficient A_2 in Equation (2) and partly to secondary scattering.

Zimm (7) has recently evaluated the coefficient A_2. For rigid spherical particles

$$A_2 = \frac{4}{\rho M},$$

where ρ = particle density,

M = mole weight.

For non-spherical particles A_2 is greater, being a function of the ratio of length to diameter. This theory predicts a slope of -8 for the lines of Fig. 4. Considerable deviation from this value is found in the case of the largest particles. This suggests that some of these particles are not spherical.

Inasmuch as the phenomenon of secondary scattering (optical diffusion) is superimposed on the usual aberrations from ideal osmotic behaviour, these conclusions with respect to particle shape must be regarded as tentative.

Finally it should be pointed out that this method is rapid and highly reproducible. Moreover, although an expensive instrument has been used for the measurements discussed here, we have found that less expensive apparatus may be used. In general any instrument capable of light-scattering measurements or its equivalent, such as a turbidimeter or nephelometer, may be employed.

Acknowledgments

The authors wish to acknowledge the work of Mr. John Wright in the surface area measurements, and the assistance of Mr. Bruce Smith and of Mr. Randall Casson.

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PRODUCTION AND PROPERTIES OF 2,3-BUTANEDIOL

XXI. CATALYTIC CRACKING OF CYCLIC ACETALS AND KETALS DERIVED FROM 2,3-BUTANEDIOL[1]

By A. C. Neish,[2] V. C. Haskell,[2] and F. J. Macdonald[2]

Abstract

Pyrolysis of the vapour of the cyclic methyl ethyl ketal of *l*-2,3-butanediol gives butanone as the chief product. Catalysts such as alumina or phosphoric anhydride greatly accelerate this reaction, while catalytic nickel has little effect. It was found necessary to have alkyl or aryl radicals substituted on the 1,3-dioxacyclopentane ring to obtain a rapid reaction. The molecule always splits symmetrically with respect to oxygen, and yields up to 90% conversion per single pass were obtained at moderate flow rates with rings substituted in the 2-, 4-, and 5-positions. The compounds tested were the formal, acetal, benzal, 2-ethylhexal, dimethyl ketal, and methyl ethyl ketal of *l*-2,3-butanediol and the *n*-butyral of ethanediol.

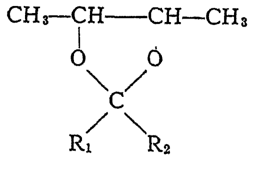
It has been shown in a previous paper (6) that 2,3-butanediol can be converted to its cyclic methyl ethyl ketal, in yields 95% of the theoretical value, merely by distilling it under reduced pressure in the presence of sulphuric acid. Because of the ease of preparation of this and other ketals and acetals (7, 9) from a fermentation product, it was thought that a study of their chemical properties would be of value.

It is known that cyclic acetals and ketals are resistant to alkaline hydrolysis but are readily hydrolysed by dilute acids; other than this there is little information in the literature on their chemical properties. The acetals of monohydric alcohols have been studied more fully. Claisen (2) found that they decomposed on heating, losing a mole of the alcohol, to give unsaturated ethers, e.g.,

$$CH_3 \,.\, CH\,(OC_2H_5)_2 \longrightarrow C_2H_5OH + CH_2 = CHOC_2H_5\ .$$

He found that the reaction was catalyzed by quinoline and phosphoric anhydride. Sigmund and Uchann (8) prepared unsaturated ethers by passing acetal vapours through a heated tube packed with nickel or porous clays. This type of reaction has been patented by Herrmann and Deutsch (3).

This paper is chiefly concerned with the pyrolysis of cyclic acetals and ketals of the general formula:



levo-4,5-Dimethyl-2R₁-2R₂-1,3-dioxacyclopentane

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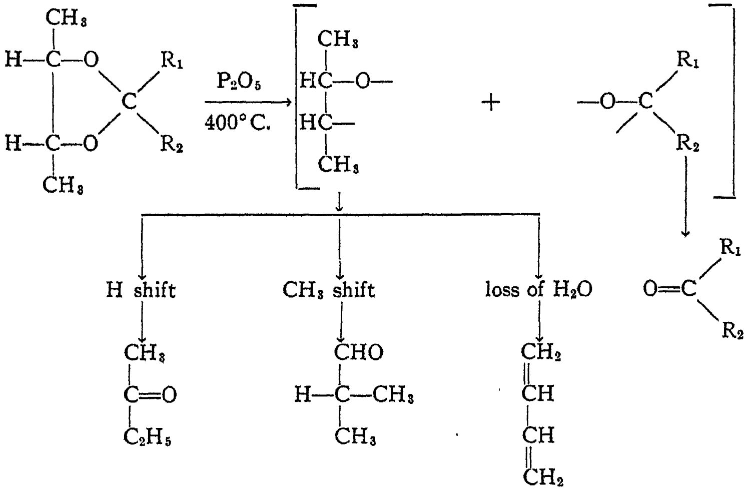
[1] *Manuscript received December 5, 1946.*

Contribution from the Division of Applied Biology, National Research Council Laboratories, Ottawa, Canada. Issued as Paper No. 49 on the Industrial Utilization of Wastes and Surpluses and as N.R.C. No. 1535.

[2] *Biochemist, Industrial Utilization Investigations.*

It has been found that the methyl ethyl ketal ($R_1 = CH_3$, $R_2 = C_2H_5$) is fairly resistant to pyrolysis in a Pyrex tube but its decomposition is greatly accelerated by alumina or phosphoric anhydride, although a catalytic nickel surface had little or no effect (see Table I). The chief product of the decomposition is butanone, particularly when phosphoric anhydride is used as the catalyst. The alumina catalyst causes formation of high boiling liquids, probably from the butanone.

The phosphoric anhydride catalyst was used for extending this work to related compounds (see Table II). The catalyst was reactivated between each experiment and in this way it was found possible to maintain its activity at an approximately constant level. In general all compounds give the same type of cleavage, i.e., the ring splits symmetrically with respect to oxygen to give butanone and the aldehyde or ketone originally used in preparing the compound. Isobutyraldehyde and easily condensed gases (butenes and butadiene) are obtained in small yields at the expense of the butanone (Table II). The general reaction may best be represented by decomposition to free radicals and rearrangement as follows:



A similar mechanism has been proposed by Bourns and Nicholls (1) to explain the formation of butanone and isobutyraldehyde during the direct dehydration of 2,3-butanediol.

It is interesting to note (Table II) that when R_1 and R_2 are light groups the cleavage takes place with difficulty and a relatively large amount of isobutyraldehyde is formed. This may mean that the shift of a H · or CH_3 · group occurs before the two fragments are completely separated and the shift of the methyl group occurs more readily when R_1 and R_2 are small for steric reasons. The slow decomposition of the formal or acetal might possibly be attributed to poisoning of the catalyst by the reactive aldehydes formed. That this is *not* so was demonstrated by passing an equimolecular mixture of the formal and methyl ethyl ketal over the phosphoric anhydride catalyst at 400° C.; the former was 1.6% decomposed and the latter to the extent of 75.4%.

Hence it may be concluded that the rate of decomposition of these compounds is accelerated by having large substituents on the ring. Under conditions similar to those used for the experiments in Table II the *n*-butyral of ethanediol was 42% decomposed in a single pass to give butyraldehyde and acetaldehyde. This shows that substituents in positions 4 and 5 of the 1,3-dioxacyclopentane ring are not necessary for this type of cleavage to occur, although they may be helpful.

Experimental

Preparation of the 1,3-Dioxacyclopentane Derivatives

The cyclic acetals and ketals of *l*-2,3-butanediol were prepared as previously described (7). The *n*-butyral of ethanediol (2-propyl-1,3-dioxacyclopentane) was prepared similarly by treating an equimolecular mixture of ethanediol and butyraldehyde with a small amount of hydrochloric acid. It was obtained as a colourless liquid (b.p. 132° C.) in a yield 73% of the theoretical value. The boiling point agrees with the value previously given for this compound prepared by a different method (4).

Pyrolysis of the 1,3-Dioxacyclopentane Derivatives

The vapour was passed at a constant known rate through a Pyrex tube at atmospheric pressure. The tube was heated by an electric furnace, the temperature being controlled by a variable transformer within ± 2° C. The heated portion of the tube had a volume of 125 ml. A constant flow of vapour was obtained by passing the liquid into a preheater at a constant rate and completely vapourizing it. The rate of flow of the liquid was controlled by a needle valve and measured with a drop-counter. A one-litre Erlenmeyer flask containing about 400 ml. served as the liquid reservoir; it was mounted high enough so the pressure in the liquid line did not decrease more than 2% during an experiment. The amount of the ketal used in each experiment (about 300 gm.) was measured by weighing the reservoir to the nearest tenth of a gram at the beginning and end of each experiment, and the rate of flow calculated by dividing this value by the time.

The products of the pyrolysis passed into a water cooled reflux condenser. A cold trap immersed in dry ice – acetone slush was connected to the top of the condenser in order to obtain easily liquefied gases. The amount of gas passing through the cold trap, if any, was measured by collection over water. In this way it was possible to measure the number of moles of gas not condensed in the cold trap, as well as the weight of liquids and easily liquefied gases.

Examination of the Easily Liquefied Gases

In one experiment (No. 6, Table I) this fraction was purified by redistillation, at room temperature and atmospheric pressure, into another cold trap cooled in dry ice – acetone slush. The small residue from this distillation was added to the liquid products. The distillate was brominated in carbon tetrachloride, starting at a temperature of −70° C. and finishing at room temperature. The solid product of the bromination was recrystallized and pure butadiene tetrabromide, m.p. 110° C., was obtained, which on mixing with an authentic sample showed no depression of the melting point. The yield corresponded to only 0.0031 mole of butadiene per mole of ketal decomposed. Distillation of the liquid bromides gave a constant boiling fraction, b.p. 83° C. (80 mm.), with a density of 1.776 and a refractive index of 1.510 at 28° C. These properties are similar to those of the 2,3-dibromobutanes. The yield was 0.008 mole per mole of ketal decomposed (25% of the liquid bromides). No other easily liquefied gases were identified. In subsequent experiments no attempt was made to analyse this fraction other than to check its boiling point, which was always in the butene–butadiene range.

Examination of the Liquid Products

The liquid products from the pyrolyses were separated by distillation through an efficient column filled with glass helices or Stedman packing. Butanone and isobutyraldehyde were identified by preparation of the 2,4-dinitrophenylhydrazones; the mixed melting points with authentic samples showed no depression. Other liquid products were identified by refractive index and boiling point. The small fractions between pure cuts were analysed approximately by determining their refractive indices. Fractionation of the higher boiling liquids (Table I) gave no pure fractions, partly because the products condense further on heating.

TABLE I

PYROLYSIS OF THE CYCLIC METHYL ETHYL KETAL OF *l*-2,3-BUTANEDIOL

Expt. No.	Catalyst	Temp., ° C.	Rate of ketal addition[1]	% Ketal decomposed	% Liquids obtained[2]	Products per mole of ketal decomposed			
						Moles of butanone[3]	Gm. of higher boiling liquids	Gm. of liquefied gases	Moles of gas
1	None	500	0.116	13.7	97.0	0.90	Nil	Nil	0.07
2	None	600	0.236	39.2	86.4	0.39	Nil	8.87	0.30
3	Ni on asbestos	400	0.530	15.5	93.5	0.91	Trace	Trace	0.29
4	Al_2O_3	300	1.021	75.0	98.7	1.49	17.0	Trace	Nil
5	Al_2O_3	380	1.138	89.4	95.7	1.39	24.4	2.3	Trace
6	Al_2O_3	450	0.568	88.5	90.9	1.25	39.8	4.8	0.20
7	P_2O_5 on pumice	400	0.328	53.2	99.0	1.99	Nil	Nil	Nil

[1] *Moles per 100 ml. of catalyst space per hr.*

[2] *Includes easily liquefied gases (caught in cold trap at −70° C. and atmospheric pressure).*

[3] *May contain a small amount of isobutyraldehyde.*

Preparation of Catalysts

The nickel catalyst was prepared by pyrolysis of asbestos soaked with nickel nitrate, followed by reduction with hydrogen. Phosphoric anhydride supported on pumice was prepared by King's method (5). It was reactivated

TABLE II

CATALYTIC CRACKING OF CYCLIC ACETALS AND KETALS OF *l*-2,3-BUTANEDIOL[1]

Reactant	Input rate[2]	Per cent decomposition	Per cent liquids obtained	Moles of products per mole of reactant decomposed[3]			
				Butanone	Isobutyraldehyde	Condensed gases[4]	Other carbonyl compounds[5]
Formal	0.463	2.7	99.8	—	—	—	—
Acetal	0.346	33.0	99.1	0.57	0.25	0.13	0.82
Dimethyl ketal	0.328	78.4	99.4	0.69	0.16	0.10	0.99
Methyl ethyl ketal	0.305	86.2	99.0	1.79	0.04	0.09	—
Benzal	0.408	80.3	98.4	0.85	0.05	0.10	0.91
2-Ethylhexal	0.297	89.0	96.5	0.65	0.08	0.15	0.90

[1] *The phosphorus pentoxide on pumice catalyst was used at 400° C. and atmospheric pressure; it was reactivated between each experiment.*

[2] *Moles per 100 ml. of catalyst space per hr.*

[3] *High boiling residues were obtained in 1 to 2% yields from each fractionation.*

[4] *Gases not condensed above −70° C. were obtained in negligible amounts. The condensed gases consist of butadiene and butenes.*

[5] *The carbonyl compound obtained is the one used in preparing the ketal; the acetal gives acetaldehyde, the dimethyl ketal gives acetone, the benzal gives benzaldehyde, and the 2-ethylhexal gives 2-ethyl hexaldehyde.*

by passing air through it at 400° C. for several hours, and then burning a piece of red phosphorus in the mouth of the tube. The batch used for the experiments reported in Table II was more active than that used for the single experiment reported in Table I. However, it was found that the activity of the catalyst (Table II) was kept fairly constant from one experiment to another by reactivation. This was checked by pyrolysing the same compound several times.

Activated alumina (Table I) was prepared by precipitating aluminium hydroxide from a solution of aluminium nitrate by ammonia. The filter cake, obtained by washing on a Büchner funnel, was dried at 150° C. and then broken up in a porcelain mortar. Particles 5 to 20 mesh were used.

Pyrolysis of Butanone in Presence of Alumina

Anhydrous butanone vapour was passed through a tube packed with the alumina catalyst (400° C.) at the rate of 1.09 moles per 100 ml. of catalyst space per hr. Twenty-three per cent was converted to other products. For each mole converted, 3.9 gm. of easily liquefied gases, 36.4 gm. of higher boiling liquids, and 0.017 mole of uncondensed gases were obtained. These products resemble those obtained from the methyl ethyl ketal of *l*-2,3-butanediol (Table I); it is quite possible that the ketal is cleaved quantitatively to butanone by the alumina catalyst and the other products are then formed from the butanone.

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THE REACTION OF CYANOGEN WITH 1,3-BUTADIENE[1]

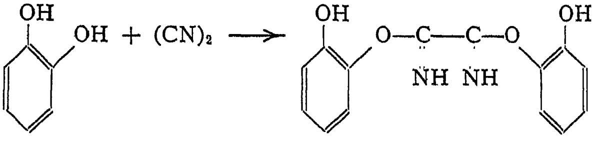
By G. J. Janz,[2] R. G. Ascah,[3] A. G. Keenan[4]

Abstract

Cyanogen and butadiene have been found to react. The main product of the reaction was identified as 2-cyanopyridine. Some 2,2′-dipyridyl and a number of unidentified compounds were also found present in the product in small yields. No evidence for the presence of β-hydromucononitrile could be found. The reaction has been studied at atmospheric pressure in the vapour phase, and in ether solution, and at superatmospheric pressures in steel or glass bombs. In all cases the course of the reaction was essentially the same, 2-cyanopyridine being the main product. The formation of 2-cyanopyridine from butadiene and cyanogen is formulated as a Diels–Alder synthesis, in which the primary adduct undergoes a dehydrogenation to yield the final product. This is the first time to our knowledge that cyanogen has been reported as a dienophile in the diene synthesis.

Introduction

There are very few references in the literature to a reaction between cyanogen and an unsaturated hydrocarbon. The chemistry of cyanogen is such as to make this an interesting field for study. Cyanogen may be regarded as the dinitrile of oxalic acid since it is formed by dehydration of oxamide, and also on hydrolysis will give oxalic acid. In many respects cyanogen and its derivatives are closely related to the halogens and their derivatives; for example, on aqueous alkaline hydrolysis of cyanogen, a cyanide and cyanate are formed just as a chloride and hypochlorite are formed by a similar hydrolysis of chlorine. Thus it seems that cyanogen may react either by virtue of its (CN) groups, or by a dissociation of the molecule. The published literature on the reaction of cyanogen with various organic compounds gives further evidence of this dual behaviour. Merz and Weith (15) reported that on reaction of cyanogen with benzene at moderately high temperatures they obtained benzonitrile. Machek (13, 14) in a study of the reaction of cyanogen with phenols claimed there was nuclear substitution, and reported that 3-cyanocatechol had been obtained from catechol and cyanogen. This was later disproved by Hahn and Leopold (9) who showed that the reaction with phenols in all cases was such that the phenolic hydroxyl group combined with the triple bond of the (—C≡N) group, and never with the (C—C) bond of the cyanogen. The reaction with catechol was shown to be



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[1] *Manuscript received June 14, 1946.*

Contribution from Canadian Industries Limited, Central Research Laboratory, McMasterville, Que.

[2] *Research Chemist. Present address: University College, London, England.*

[3] *Research Chemist.*

[4] *Research Chemist. Present address: National Research Laboratories, Ottawa, Canada.*

The reaction of cyanogen with diazomethane reported by Azzarello (2) to give cyanosotriazol is of interest since in this case the (—C≡N) group of the cyanogen is found as part of the ring structure in the final product. Tollens and his associates (18, 19) reported an attempt to add cyanogen to a double bond. By prolonged bubbling of cyanogen through allyl alcohol, an oil was obtained the analysis of which corresponded to $C_3H_5(CN)_2OH$. Among the products obtained on its hydrolysis they reported oxamide, and it would seem that the (C—C) bond of the cyanogen was not broken in the formation of this compound.

It seemed reasonable therefore to expect either a straight chain addition product, a cyclic addition product, or both from a reaction of cyanogen and butadiene. The primary object of our investigation was to attempt the reaction of cyanogen with butadiene. When it was found that a reaction occurred, the work was extended to determine the effect of reaction variables on the course of the reaction.

Experimental

Materials

For the laboratory preparation of cyanogen a modification of Hahn and Leopold's apparatus (9) was used for the reaction between sodium cyanide and copper sulphate. The hydrogen cyanide in the gas was absorbed in aqueous silver nitrate and the moisture was removed by phosphorus pentoxide towers. The dry cyanogen was finally condensed at −80° C. It was stored in a steel pressure cylinder at room temperature. It has been found that if the cyanogen is pure and dry it may be maintained safely thus for several months.

The butadiene was that obtained from the Matheson Company and was used without further purification.

Apparatus

The reaction was studied at atmospheric pressure in the vapour phase, and in ether solution, and at superatmospheric pressures in steel and glass vessels.

For the vapour phase study the size of the reactor varied from a small all-glass system used for the scouting work to a large steel reactor used for the more detailed study of the reaction conditions. The arrangement of the reactor and the rest of the apparatus is shown in Fig. 1. For the temperature–time series of experiments the reactor was made from a 2 in. steel pipe, 21 in. long, with a thermocouple well of $\frac{1}{4}$-in. pipe extending down the centre of the large pipe, and a removable flange head on the bottom. The volume of the reaction chamber *E* was 920 ml. It was covered with two layers of asbestos sheet, and then wound in three sections with nichrome resistance spirals, each being 30 ohms (0.665 Ω/ft.), and finally thermally insulated with a heavy piece of asbestos steam pipe lagging. This steel reactor was used for all runs of 10 to 150 sec. contact times. For exceedingly short contact times, one second or less, a silica reactor was used. It was made from a silica tube

20 in. long, and 0.25 in. inside diameter, and was also electrically heated. Temperature measurements were made with a chromel–alumel thermocouple and an L. & N. potentiometer indicator. Table I gives representative values of the temperature gradient in the reactor during three different trials; the measurements start from the bottom of the thermocouple well.

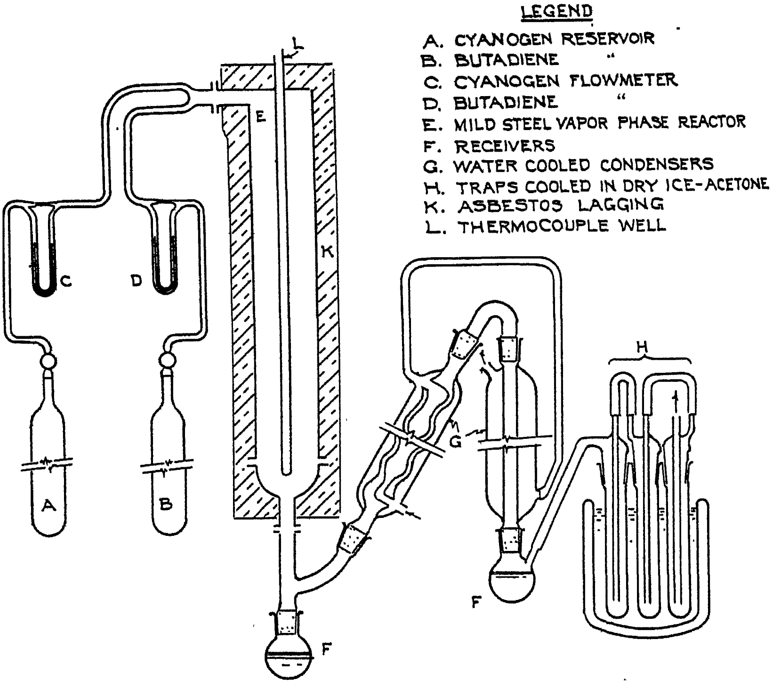


FIG. 1. *The arrangement of the apparatus for the vapour phase study.*

TABLE I

TEMPERATURE GRADIENT OF 2 IN. MILD STEEL REACTOR

Position of thermocouple, in.	0	2	4	6	8	10	12	14	16	18	20
Temperature, °C. (1)	539	607	650	664	666	666	664	664	661	642	593
(2)	481	542	579	586	586	586	586	586	584	570	528
(3)	379	440	471	478	480	480	485	490	485	471	443

The gas reservoirs were small steel laboratory gas cylinders fitted with sensitive needle valves. The flowmeters were of the standard constriction type, and each was calibrated with the gas being used with it. A saturated aqueous solution of sodium chloride containing 10 cc. concentrated hydrochloric acid per litre (17) was used as the indicator liquid for the cyanogen flowmeter, and corn oil for the butadiene flowmeter. For cooling the gases and stripping out the reaction product, two water cooled condensers were used. Finally the unreacted butadiene and cyanogen and more volatile products were condensed at −80° C.

A few experiments were made with butadiene and cyanogen under superatmospheric pressures to observe the course of the reaction under these conditions. The apparatus used consisted of glass bomb tubes, a stainless steel bomb, and the standard high pressure AMINCO hydrogenation equipment.

Procedure and Results

1. *The Reaction of Cyanogen with Butadiene*

(i) *The Reaction*

Cyanogen and 1,3-butadiene in a molar ratio of 1.0 : 1.0 were passed through the vapour phase reactor for a total time of 13 hr. The temperature of the reactor was maintained at about 480° C., and the contact time of the gases in the reaction zone was about 98 sec. The total recovery, as liquid product and unreacted butadiene and cyanogen, was about 84.5% by weight of the initial material input. The yield of product, stripped from the gases leaving the hot reaction zone by the water-cooled condensing system, was about 38.5% by weight, calculated on the total input of butadiene and cyanogen. After removing the more volatile portions, fractional distillation at 8 to 12 mm. of mercury pressure in a Whitmore–Fenske column was used to investigate the crude liquid product. It was separated into three fractions; (*a*) a low boiling fraction, (*b*) an intermediate boiling fraction, about 47% by weight of the crude product, and (*c*) a high boiling fraction.

(ii) *The Reaction Products*

The intermediate boiling fraction (*b*) above was identified as 2-cyanopyridine. It was separated from the crude product by fractional distillation, as mentioned above, and further purified by filtering off the crystals at 0° C., and then washing and recrystallizing several times from cold ether. The physical properties found for our product and for those quoted in the literature for 2-cyanopyridine are: m.p. obs. 27.0° to 27.5° C., lit. 29° C., 26° C., (4); b.p. found 222° to 227° C., lit. 212° to 215° C. (4), 222.5° to 223.5° C. (7). Found: C, 70.00; H, 4.07; N, 26.04%. Calc. for $C_6H_4N_2$: C, 69.22; H, 3.87; N, 26.91%. In order to identify this product, picolinic acid hydrochloride was prepared by subjecting the 2-cyanopyridine to hydrolysis with aqueous sodium hydroxide and separating the acid as the hydrochloride. The results of the analysis for the picolinic acid hydrochloride were as follows: Found: C, 45.44; H, 4.21; N, 8.55; Cl (ionic), 21.83; (total), 21.95%. Calc. for $C_6H_6NO_2Cl$: C, 45.15; H, 3.79; N, 8.78; Cl, 22.23%. From the picolinic acid hydrochloride prepared in this manner, the free picolinic acid was prepared by mixing with a half molar equivalent of barium hydroxide and extracting the free acid with chloroform. The picolinic acid thus isolated, after recrystallization from dioxane, and sublimation, was found to have a melting point of 135° to 136° C. (lit. 136° to 137° C. (10), 134.5° to 136° C. (4)). By heating the 2-cyanopyridine with lime, pyridine was separated from the mixture by distillation (b.p. found 114.7° C.; lit. 115.3° C.; N_D^{26} found 1.505, lit. 1.507). The pyridine was further identified by comparing the X-ray diffraction pattern of its picrate with that from an authentic sample of pyridine.

A particular effort was made to detect the presence of β-hydromucononitrile (b.p. 110° C. (2 mm.); m.p. 74° to 75° C. (6)) in the low and high boiling fractions of the reaction product. The low boiling fraction included all the distillate taken off before the 2-cyanopyridine fraction, the upper limit in distillation range generally being about 70° C. at 2 to 3 mm. pressure. From the vapour phase runs at the lower temperatures (up to 500° C.) the low boiling fraction was found to be mainly 4-vinylcyclohexene. Careful fractionation of a low boiling fraction from a run at 600° C. indicated that it was composed of several liquids boiling in the range of 55° to 210° C. (760 mm.), and with very little 4-vinylcyclohexene present. The more complex nature of this fraction at the higher temperatures is to be expected since 4-vinylcyclohexene is unstable at temperatures above 500° C. (3), and since aromatic compounds are formed from butadiene at high temperatures (11). Investigation of the fraction of the crude product boiling higher than 2-cyanopyridine established the presence of 2,2′-dipyridyl. It was separated in the Whitmore–Fenske column at 133° to 134.5° C. (11 mm.), and was found to have the following properties: m.p. (impure) 56.6° C.; b.p. 270° to 272° C. (760 mm.); picrate, m.p. 154° to 155.5° C.; gave characteristic rose red colour reaction with ferrous ions (lit. for 2,2′-dipyridyl, m.p. 69.5° C., b.p. 272.5° C. (760 mm.); picrate m.p. 154° to 155.5° C.; gives characteristic rose red colour reaction with ferrous ions). Two other products *A* and *B* were also isolated from the high boiling fractions of the high temperature runs (700° C.), but were not further investigated when it was found that they were not β-hydromucononitrile. Unknown *A*, (b.p. 77° to 80° C. (3 mm.), m.p. 71° to 72° C., N analysis 23.4%) was not β-hydromucononitrile (m.p. 74° to 75° C., N calc. 26.4%) because the mixed melting point was considerably depressed, and the X-ray diffraction patterns of the two were quite different. The unknown probably is 2-cyano-2-picoline (m.p. 87.5° to 88° C., N calc. 23.7%) since the mixed melting point of these two was around 76° to 81° C., and the X-ray diffraction pattern of these two was identical. Unknown *B* was found to have a melting point of 185° to 190° C., and obviously was not β-hydromucononitrile.

2. *The Temperature–Contact Time Study of the Vapour Phase Reaction*

The temperature range of 400° to 700° C. and the contact time range of 0.5 to 120 sec. were investigated. A standard procedure was used for this series of experiments. The reactants were introduced in approximately equimolar proportions. During the run the rate of input of gases was followed by the flowmeter readings, and the temperature of the reactor at the 12 in. mark was observed every 15 min. The total temperature gradient was generally checked twice during a trial. The analysis of the crude product was carried out by a distillation at reduced pressure in a Whitmore–Fenske column. The data of these runs are given in Table II.

TABLE II

DATA ON THE REACTION OF BUTADIENE AND CYANOGEN IN THE VAPOUR PHASE

Temp., °C., (approx.)	Duration of runs, hr.	Contact time, sec.	Reactant ratio butadiene: cyanogen, moles	Total material recovery, % of input by weight	Crude liquid product, % of input by weight	2-Cyano-pyridine, % of crude product by weight	2-Cyano-pyridine, % of input by weight
470–490	1.66	23	1.28 : 1.0	85.5	18.7	33	6.17
470	2.5	69	0.93 : 1.0	67	30.5	39	11.9
480	13.0	98	1.0 : 1.0	84.5	38.5	47	18.1
700	3.0	0.39	1.0 : 1.0	77.6	13–14	41.5	5.6
700	12.5	0.88	1.15 : 1.0	55	29.7	27	—
700	1.5	18	1.18 : 1.0	45	27	23	6.3
700	17.5	32.5	0.97 : 1.0	54	43.9	24	10.5
700	9.6	33	0.89 : 1.0	58	43	24	10.3
680	8.0	37	0.77 : 1.0	53.7	36.6	33	12.1
700	2.75	90	0.82 : 1.0	39	34	16	5.5

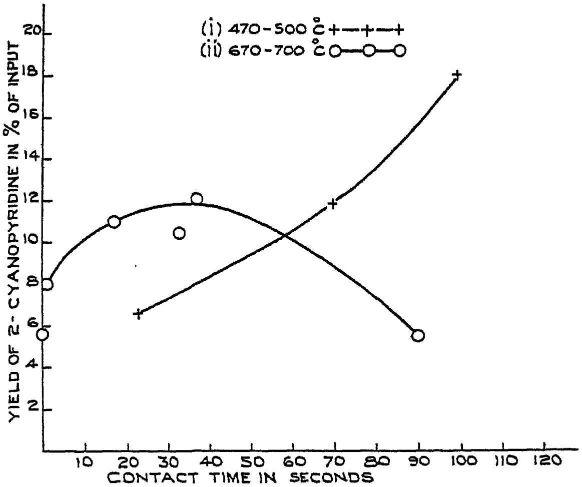


FIG. 2. *The relation between yield of 2-cyanopyridine and contact time.*

The relation between the yield of 2-cyanopyridine and the contact time is most clearly seen by considering the results graphically in Fig. 2.

In the temperature range of 470° to 500° C., it seems that the yield of 2-cyanopyridine increases with increasing contact time. The best yield, 18.1% of 2-cyanopyridine per gram input reactants, is obtained using a contact time of 98 sec. From the curve it seems that this yield would probably increase with an increase in contact time. Pyrolysis of the products and reactants could also be expected to increase with increasing contact time, and this effect may become great enough to swamp any increase in yield of 2-cyanopyridine. This trend was indicated when contact times over 200 sec. were employed.

The effect just mentioned is clearly evident from the results in the temperature range of 670° to 700° C. This curve shows that the yield of 2-cyanopyridine increases with increasing contact time to a maximum of about 12.1% when the contact time has reached 36 sec. At longer contact times the yield drops, probably because the pyrolysis effect is masking any increase of yield in 2-cyanopyridine.

The results of the yield–temperature study are also presented graphically in Fig. 3 to show the relation between the yield of 2-cyanopyridine and the temperature of the reaction zone more clearly.

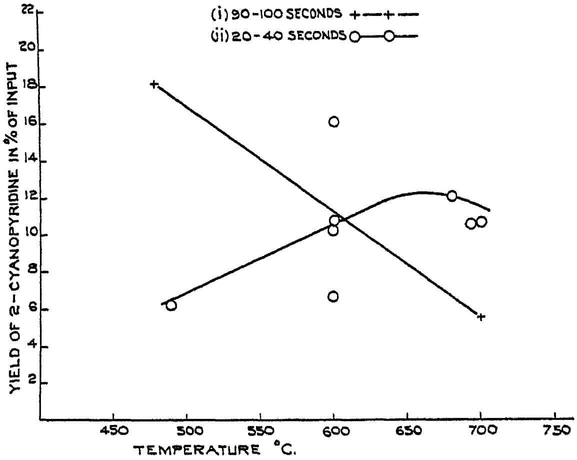


FIG. 3. *The relation between yield of 2-cyanopyridine and temperature of reaction zone.*

Using a relatively long contact time (90 to 100 sec.) the yield of 2-cyanopyridine is greatest (18.1%) at about 480° C., and decreases with increasing temperature to a value of about 5% at 700° C. This curve probably shows the effect of pyrolysis at high temperatures more clearly than the previous graph. At shorter contact times (20 to 40 sec.) the yield of 2-cyanopyridine increases with increasing temperatures from about 6% at 480° C. to about 12.1% at 680° C. The lower yields at 700° C. probably indicate that the pyrolysis effect is becoming great enough to mask any increase in yield of 2-cyanopyridine.

In the region investigated, the optimum conditions would seem to be a temperature of about 480° C., and a contact time of about 90 to 100 sec.

3. *The Vapour Phase Reaction in the Presence of Hydrogen*

Since the formation of 2-cyanopyridine from butadiene and cyanogen is postulated as involving a dehydrogenation, the vapour phase reaction was carried out in the presence of hydrogen to see if the course of the reaction would be altered. The apparatus and set-up for this study was modified only to permit the introduction of hydrogen gas along with the mixture of reactants. A series of runs was made with the ratio of butadiene to cyanogen being about equimolar while the hydrogen to butadiene or cyanogen ratio was varied from five to one, to approximately equimolar. The reaction product was investigated in the usual manner. In Table III the operational data and experimental results for these experiments are listed.

TABLE III

DATA ON THE REACTION OF BUTADIENE AND CYANOGEN IN PRESENCE OF HYDROGEN

Trial	Temp., °C. (approx.)	Contact time, sec.	Molar ratio of gases			Material recovery	Crude yield
			H_2 :	Butadiene :	Cyanogen	% by weight calc. on input of butadiene and cyanogen	
(1)	470	22	5.03	1.05	1.0	82	0
(2)	470	24	1.4	1.1	1.0	84	7
(3)	470–490	23	0	1.28	1.0	85.5	18.7

No reaction was observed with a large excess of hydrogen present. With a more nearly equimolar ratio of gases a slight reaction was observed. Two similar trials were made at 700° C., and here, with approximately an equimolar ratio of the gases, the crude product was obtained in 33% yield, while with a threefold excess of hydrogen, only a 12% yield was obtained.

Examination of the crude product by distillation indicated that it was essentially the same as that obtained from the reaction in the absence of hydrogen, i.e., contains about 20% 2-cyanopyridine. The high boiling fraction however had a reddish colour instead of the usual yellow-green, and distillation yielded a series of fractions boiling over ranges of 10° C. or greater, which were not further investigated.

For purposes of comparison, the results of an experiment without hydrogen are listed in Table III. To see if the decrease in yield was due mainly to a dilution effect of the butadiene and cyanogen by hydrogen, two more experiments were made. The conditions for these runs were identical to those used in Runs 1 and 2, but instead of hydrogen, nitrogen (an inert gas) was used. There was no product formed when the nitrogen was used in fivefold excess to the others, and only a 10% yield of crude product when the nitrogen was decreased as in Run 2. The decrease in yield observed above is apparently due to a dilution effect of the butadiene and cyanogen by the third gas.

4. *The Vapour Phase Reaction in the Presence of Catalysts*

The question of a catalyst for this reaction has not been investigated to any great extent. The only catalysts tried were silica gel and 'Florex'. For these experiments a small all-glass reactor, similar in design to the large steel reactor, was used, with the rest of the experimental set-up about the same. The reaction in the presence of 'Florex' was carried out at 470° to 485° C. The product was a moist brown solid from which a small amount of red oil could be extracted. When silica gel was used, the reactor was operated in the range 100° to 300° C. and at 400° C. In both cases the catalyst became quite black and at 400° C. a moist brown solid product was also obtained. Two brands of silica gel, 'Davco' and 'Hyposil', were used. The brown solid was found to be quite soluble in concentrated sulphuric acid, and probably was paracyanogen (4).

From the above results it seems that silica gel and 'Florex' promote only a simultaneous decomposition and polymerization of cyanogen, and do not catalyze the formation of 2-cyanopyridine.

5. *The Reaction under Superatmospheric Pressures*

Several trials were carried out in glass bomb tubes at about 100° C. Butadiene and cyanogen, about 5 to 7 gm. each, were sealed in glass and heated for periods varying from 21 to 33 hr. in a furnace at 100° ± 10° C. From these there was recovered unreacted butadiene and cyanogen and an oil (21 to 31% yields). This oil contained about 55% by weight of 2-cyanopyridine, the remainder being mainly 4-vinylcyclohexene. When the trial was carried out in a steel bomb, fitted with a pressure gauge, a similar product was obtained at 105° C. The pressure developed in the vessel was 440 lb. per sq. in. One trial was made at 250° C., a temperature above the critical temperatures of both reactants. The high pressure AMINCO equipment was used for this work. The bomb was charged with 52 gm. of cyanogen, and 51 gm. of butadiene, and heated for a period of six hours to a maximum temperature of 270° C. The pressure rose to a maximum of 620 lb. per sq. in., and settled to a final value of 200 lb. per sq. in. The product was a black solid mass (62 gm.) from which a brown oil could be extracted (31 gm.).

Analysis of the oil by distillation showed it to be mainly vinylcyclohexene, and 2-cyanopyridine (26%).

The work in the bomb tubes indicates that the reaction of butadiene and cyanogen is essentially the same under superatmospheric pressures as at atmospheric pressures. The black solid product observed in these experiments was not investigated, but probably contains a considerable amount of paracyanogen (5).

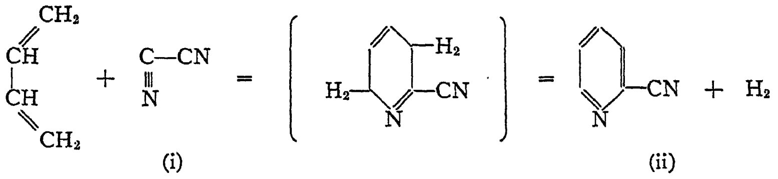
6. *The Reaction in Ether Solution*

There are some references (9, 18) to the reaction of cyanogen with organic compounds in an inert solvent. It was of interest therefore to attempt the reaction of cyanogen and butadiene in ether solution at room temperature. Slow streams of butadiene and cyanogen were bubbled, under slight pressure, through about four litres of vigorously stirred ether. After some 47 hr. the experiment was stopped and the reaction mixture distilled. The high boiling residue remaining after all the solvent had been removed contained no combined nitrogen.

Butadiene and cyanogen apparently do not react in ether solution at room temperature.

Discussion

To account for the formation of 2-cyanopyridine, the reaction between cyanogen and butadiene may be formulated as:

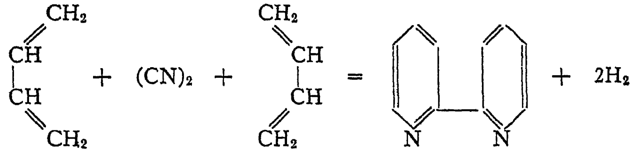


The first step of this involves a diene synthesis, well known as the Diels–Alder reaction, and the second a dehydrogenation of the adduct to give the final product. This is the first time to our knowledge that cyanogen has been reported as capable of acting as a dienophile in Diels–Alder reactions.

To date, the dienophiles in the generalized diene synthesis have been grouped into the following types, $C{=}C{-}R$ and $C{\equiv}C{-}R$, in which R may be of the type that terminates in the carbonyl, acetonyl, nitro, sulphonyl, cyano, amino, or vinyl group, or even hydrogen, attached directly to one of the olefinic or acetylenic groups (16). An earlier investigation has shown that cyanobenzene can act as a dienophile although the authors did not point this out (8). The reaction involved was the preparation of pentaphenylpyridine from tetracyclone and cyanobenzene. The phenyl group served as R, and ($C{\equiv}N$) was the dienophilic component. By the work presented in the present report it has been shown that when R is the cyano group, the dienophylic component may be the ($C{\equiv}N$) group.

In this reaction, the intermediate adduct probably first formed is unstable under the conditions of the reaction, and by losing hydrogen forms 2-cyanopyridine. It is not unusual in a diene synthesis that, for a slowly reacting system, elevated temperatures and pressures must be used. The application of high temperatures to accelerate the reaction has its limits, however, because the diene synthesis is a reversible reaction, and in the case of exothermic reactions, equilibria are set up which are displaced more and more to the side of the reactants with increasing temperatures. As indicated above, however, the diene adduct spontaneously changes to a dehydrogenated product, and it may be this step that makes this synthesis possible at the high temperatures used.

The presence of 2,2′-dipyridyl in the reaction of cyanogen and butadiene may be explained by a possible reaction of two moles of butadiene with one of cyanogen, as follows:



by a mole of butadiene with 2-cyanopyridine.

From the experimental work it would seem that at temperatures less than 400° C. at atmospheric pressure the rate of reaction rapidly becomes so slow that no reaction is observed. At higher temperatures no straight chain addition product but rather 2-cyanopyridine was found. The catalyst search for this reaction was not pressed when it was suspected that a Diels–Alder synthesis was involved, since such a reaction is not sensitive to catalytic effects (1). It may be, since the reaction as postulated also involves a dehydrogenation, that the use of a suitable dehydrogenation catalyst in the optimum temperature range might affect the rate of the over-all reaction.

The results of this research have been covered in a recent patent (12).

Acknowledgment

The authors are indebted to J. H. Michell for the identification of 2-cyanopyridine and 2,2′-dipyridyl in the product.

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THE PREPARATION OF 2-CYANOPYRIDINES FROM CYANOGEN AND SOME SIMPLE 1,3-DIENES[1]

By G. J. Janz[2] and A. G. Keenan[3]

Abstract

In a previous paper, it was shown that cyanogen could be reacted with butadiene to give 2-cyanopyridine as the main reaction product. It was postulated that the reaction occurred through a Diels–Alder type of mechanism, with spontaneous dehydrogenation of the primary adduct. The present investigation has extended this study to the reaction of cyanogen with (i) isoprene, (ii) chloroprene, (iii) 2-methylpentadiene, and (iv) hexachlorobutadiene. The results are consistent with the mechanism postulated in the earlier paper.

Introduction

On studying the reaction between cyanogen and butadiene, it was found (7) that the main product of the reaction was 2-cyanopyridine. The formation of this product was explained as being due to a Diels–Alder reaction between cyanogen and butadiene, in which the primary adduct underwent a dehydrogenation to yield the final product. The role of cyanogen as a dienophile was novel. The primary object of the present research was to see if this behaviour of cyanogen could be generalized for other simple 1,3-dienes, namely, (i) isoprene, (ii) chloroprene, (iii) 2-methylpentadiene, and (iv) hexachlorobutadiene.

Experimental

MATERIALS

Isoprene.—This was prepared from dipentene in 20% yields by pyrolysis. A nichrome wire spiral maintained at a dull red heat was suspended in the vapours of dipentene refluxing under a vacuum of 2 to 3 cm. of mercury (3, 6). The gases given off were passed through water cooled scrubbing towers and condensed in dry ice – acetone traps. The product from the pyrolysis was distilled in a Whitmore – Fenske column at atmospheric pressure. The fraction boiling from 34° to 38° C. was collected as isoprene (b.p. 34° C.). At least 95% of this fraction boiled in the range 34.5° to 35.5° C. The isoprene was prepared a few days before use and stored in a small steel cylinder provided with a needle valve.

Chloroprene (2-Chlorobutadiene-1,3).—This was received from E. I. du Pont de Nemours and Company in the form of a 50% solution in xylene containing a small amount of catechol as a stabilizer. It was distilled in a nitrogen atmosphere under a vacuum of 12 to 15 cm. through an 11 in. glass column

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Contribution from Canadian Industries Limited, Central Research Laboratory, McMasterville, Que.

[2] *Research chemist. Present address: University College, London, England.*

[3] *Research chemist. Present address: National Research Laboratories, Division of Chemistry, Ottawa, Canada.*

packed with Berl saddles. The distillate was partly condensed in a water cooled receiver and more completely in a series of dry ice - acetone traps. Under atmospheric pressure the product boiled at 60° C. (lit. 59.4° C.).

2-Methylpentadiene-1,3.—This was obtained from E. I. du Pont de Nemours and Company and used without further purification.

Hexachlorobutadiene.—This was obtained as a sample from the Hooker Electrochemical Company. It was a colourless liquid, b.p. 210° to 220° C., f.p. $-20°$ to $-25°$ C., and formula $CCl_2=CCl-CCl=CCl_2$.

Cyanogen.—This was prepared from sodium cyanide and copper sulphate, as described previously (7).

APPARATUS

The reactor used for the reaction of cyanogen with isoprene, chloroprene, and 2-methylpentadiene, was the mild steel reactor used for the vapour phase study of the reaction of cyanogen with butadiene (7). The experimental set-up was exactly as described (7) except that the method of feeding the dienes had to be somewhat modified. For the work with isoprene, a steam jacketed flowmeter was used, and the isoprene cylinder was immersed in a water bath maintained at 65° C. When chloroprene was used, it was fed as a liquid from a calibrated dropping funnel into a vaporizer maintained at 100° C. From this vaporizer the reactants (cyanogen and chloroprene) were led into the reactor. The same system was used for 2-methylpentadiene.

The reaction between hexachlorobutadiene and cyanogen was not tried in the vapour phase at atmospheric pressure, but only in glass bomb tubes at superatmospheric pressures.

PROCEDURE

(*i*) *Cyanogen and Isoprene*

(*a*) *The Reaction*

With the reactor maintained at 490° C. at the 12 in. mark, isoprene and cyanogen were passed through for 155 min. at the rates of 21.4 and 15.4 gm. per hr., respectively (molar ratio 1 : 1). The contact time at these rates was about 90 sec. The crude product (a black pasty mass that set to a solid at 0° C.) was produced at the rate of 13.5 gm. per hr. This represents a material loss in the reaction of 38%. This crude product was shown by the reactions described below to contain at least 29.3% of cyanopicolines. Hence the latter were produced in at least 18% yield calculated on the total input of reactants.

(*b*) *The Identification of the Product*

The black crude product was distilled under vacuum in a Vigreux flask. This gave, among other fractions, one that boiled at 88.5° C. (2 mm.) and was a solid under ordinary conditions. Three crystallizations from ligroin gave a product melting at 48° to 77° C. This impure material gave the following analysis. Found: C, 71.18; H, 4.7; N, 23.4%. Calc. for $C_7H_6N_2$: C, 71.15; H, 5.12; N, 23.7%. This corresponds quite well to a cyanopicoline. This material was hydrolysed by refluxing with aqueous sodium hydroxide and then decarboxylated by dry distillation with lime. The resulting liquid yielded on distillation a fraction boiling from 143° to 148° C. at atmospheric pressure. Mixtures of 3- and 4-picoline boil in the range 142° to 146° C. The above fraction was treated according to the procedure for separating 3- and 4-picolines through their zinc chloride salts (1, 5). The zinc chloride salt, after two recrystallizations from ethanol, was decomposed with potassium hydroxide to yield a colourless oil. The latter formed a yellow crystalline picrate which, after two crystallizations from ethanol, had a melting point of 161° to 162° C. The analysis was found to check well for picoline picrate. Found: C, 44.34; H, 2.77; N, 17.1%. Calc. for $C_{12}H_{10}N_4O_7$: C, 44.73; H, 3.13; N, 17.4%. According to the literature the melting point of 4-picoline picrate is 163° to 164° C., 167° C. (2), and 158° to 161° C. (1). A sample of authentic 4-picoline (Eastman Kodak Company) gave a picrate of melting point 163.5° to 164.5° C. The X-ray diffraction pattern of this picrate was identical with the one prepared from the unknown picoline.

From another decarboxylation of the crude product (m.p. 48° to 77° C.), the oil (b.p. 142° to 145° C.) was isolated and treated according to the procedure for the separation of the 3- and 4-picolines through their oxalates (9, 10). Three crystallizations gave an oxalate (m.p. 137.5° to 139° C.) that corresponded to the 4-picoline oxalate (lit. m.p. 139° to 140° C. (9), 137° to 138° C. (10)). Repeated crystallizations of both the oxalate and picrate formed from this fraction gave further products which were identified as 4-picoline derivatives. No evidence could be found for the presence of the 3-picoline derivative.

The original crude product (m.p. 48° to 77° C.) was further recrystallized repeatedly from ligroin. This yielded a white solid with a sharp m.p. of 87° to 88° C. and which gave an analysis that checked well for a cyanopicoline. Found: C, 71.80; H, 5.16; N, 23.6%. Calc. for $C_7H_6N_2$: C, 71.15; H, 5.12; N, 23.7%. This pure substance comprised well over 50% of the initial solid.

From this evidence we conclude that one product of the reaction between cyanogen and isoprene is 2-cyano-4-picoline. The presence of an isomeric cyanopicoline in the impure recrystallized product (m.p. 48° to 77° C.) is indicated by the over-all analysis. No attempt was made to elucidate its structure.

(*ii*) *Cyanogen and Chloroprene*

(*a*) *The Reaction*

The chloroprene and cyanogen were fed into the reactor at 20 gm. per hr. and 12 gm. per hr. respectively (molar ratio 1 : 1). The temperature was 500° C. and the contact time of the gases in the reaction zone was about 110 sec. The crude product was produced at the rate of about 9 gm. per hr. The total recovery as crude product and unchanged reactants was about 63%.

(*b*) *The Identification of the Product*

A fraction boiling at 140° C. (30 mm.) was separated from the product by distillation in a Vigreux flask. This fraction (about 15% by weight of the crude) crystallized to a green solid at room temperature. After several crystallizations from ether and ethanol, a white solid was obtained of melting point 107.5° to 108° C. Found: C, 51.86; H, 2.40; N, 20.55; Cl, 25.73%. Calc. for $C_6H_3N_2Cl$: C, 52.01; H, 2.18; N, 20.22; Cl, 25.59%. Hence this checks well for a chlorocyanopyridine.

From the reactor a black tarry mass was also recovered. It was extracted with ether, and the solid thus recovered was recrystallized twice from ethanol. This yielded a white crystalline material of melting point 83° to 84° C. Found: C, 51.92; H, 2.42; N, 20.1; Cl, 26.0%. Calc. for $C_6H_3N_2Cl$: C, 52.01; H, 2.18; N, 20.22; Cl, 25.59%. This also checks for a chlorocyanopyridine. This solid was hydrolysed with alcoholic (75% ethanol) sodium hydroxide solution. The reaction mixture was acidified with hydrochloric acid, evaporated to dryness, and the residue crystallized from water. A brown solid was obtained which darkened at 170° C. and melted with decomposition at 172° C. (lit. for 5-chloropicolinic acid, m.p. 169° to 170° C. (4) and 168° C. (2)).

One product of the reaction of cyanogen with chloroprene has thus been shown to be 5-chloro-2-cyanopyridine (m.p. 83° to 84° C.). An isomeric chlorocyanopyridine (m.p. 107.5° to 108° C.) also appears to be formed but its structure was not investigated further.

(*iii*) *Cyanogen and 2-Methylpentadiene*

(*a*) *The Reaction*

The cyanogen and 2-methylpentadiene were fed in at the rates of 13.2 gm. per hr. and 17.9 gm. per hr., respectively (molar ratio approximately 1 : 1). The reaction temperature was about 500° C., and the contact time about 121 sec. The total recovery, as crude product and unreacted materials, was 75% of the input and the crude product alone was about 61% of the input.

(*b*) *The Identification of the Product*

The crude product was filtered free of unreacted 2-methylpentadiene, and the resulting solid was recrystallized repeatedly from ligroin. A white crystalline material was thus obtained, with a melting point of 53° to 53.5° C. Found: C, 73.0; H, 6.1; N, 20.8%. Calc. for $C_8H_8N_2$: C, 72.7; H, 6.1; N, 21.2%. This corresponds well to a cyanolutidine. The yield was approximately 30%, calculated on the input. This material was hydrolysed in the usual manner with aqueous sodium hydroxide and then decarboxylated by dry distillation with lime. From this a liquid, boiling from 156° to 157° C. at atmospheric pressure, was isolated (lit. for 2,4-lutidine, b.p. 157° C., 159° to 159.5° C. (2)). From this oil a picrate was formed which, after recrystallization from ethanol, had a melting point of 179° to 180° C. (lit. for picrate of 2,4-lutidine, 179° C. (2)). This checks well for the 2,4-lutidine derivative.

It appears therefore that 6-cyano-2,4-lutidine is a product of the reaction of cyanogen with 2-methylpentadiene. No evidence for the formation of isomers was obtained in this case.

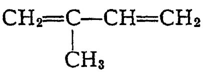
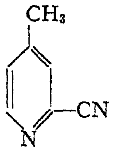
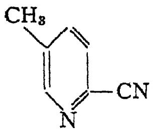
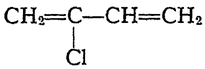
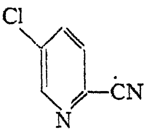
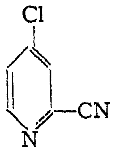
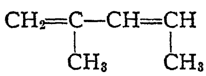
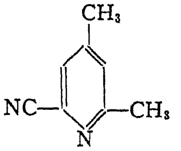
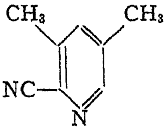
(iv) Cyanogen and Hexachlorobutadiene

In an attempt to react cyanogen and hexachlorobutadiene, approximately equimolar quantities of the two were sealed in glass bombs and heated in a furnace for 46 hr. at 150° to 170° C. About 86% of the hexachlorobutadiene was recovered unreacted. A small amount of black solid, similar to that observed in the high pressure work with cyanogen and butadiene (7), was also formed. No other solid reaction products were found. The experiment was repeated using reaction conditions of 37 hr. at 210° C. and 66 hr. at 230° C. In each case nearly all the hexachlorobutadiene was recovered unreacted and no evidence of addition products was found.

Discussion

Under the conditions investigated, cyanogen reacts with isoprene, chloroprene, and 2-methylpentadiene, apparently through the triple bond of the CN group, forming substituted pyridines. On the assumption that no nuclear migration of the CN group takes place during the reaction, a substituted 2-cyanopyridine has been identified among the reaction products in each case.

If, as postulated in our earlier paper (7), we assume that the formation of these substituted pyridines occurs through a Diels–Alder type of mechanism with spontaneous dehydrogenation of the primary adduct, then each reaction would be predicted to give rise to two isomeric substituted 2-cyanopyridines. The table below gives, in the first column, the formula of the compound reacted with cyanogen and in the second and third columns, the formulas of the two predicted isomeric products.

(i)  $CH_2{=}\underset{\underset{CH_3}{\vert}}{C}{-}CH{=}CH_2$ Isoprene	 2-Cyano-4-picoline	 2-Cyano-5-picoline
(ii)  $CH_2{=}\underset{\underset{Cl}{\vert}}{C}{-}CH{=}CH_2$ Chloroprene	 5-Chloro-2-cyanopyridine	 4-Chloro-2-cyanopyridine
(iii)  $CH_2{=}\underset{\underset{CH_3}{\vert}}{C}{-}CH{=}\underset{\underset{CH_3}{\vert}}{CH}$ 2-Methylpentadiene	 6-Cyano-2,4-lutidine	 6-Cyano-3,5-lutidine

In the experimental section of this paper, the compound given in the second column of the above table was, in each case, identified among the products of each respective reaction. In the case of the first two reactions, evidence was also obtained for the presence of an isomer but its structure was not investigated. As in the previous paper (7), no attempt was made to identify hydrogen in the off-gas from the reaction.

In the literature on the Diels–Alder reaction (11), it is reported that dienophiles will not add to halogenated dienes of the structure Cl−C=C−C=C or C=C (Cl)−C (Cl)=C, but will add to dienes of the structure C=C (Cl)−C=C if there are no other chlorine atoms in the molecule. Our results with cyanogen and chloroprene on the one hand, and hexachlorobutadiene on the other, are in accord with this.

The reactions of cyanogen with the 1,3-dienes mentioned in this paper are thus seen to be not inconsistent with predictions based on a postulated Diels–Alder mechanism, with spontaneous dehydrogenation of the primary adduct at the temperature of the reaction.

The results of this research have been covered in a recent patent application (8).

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THE PREPARATION OF CYANOGEN CHLORIDE[1]

BY H. W. BARNETT,[2] R. G. DAVIS,[3] AND R. P. GRAHAM[4]

Abstract

A detailed description is given of a laboratory method for the preparation of cyanogen chloride. The method involves the action of chlorine on a solution of zinc sulphate and sodium cyanide, the reaction being carried out under carefully controlled conditions. The procedure described has been found to give a pure product in yields close to 70% of the theoretical.

Introduction

Cyanogen chloride, a colourless gas at normal temperatures, was apparently first prepared about 150 years ago by Berthollet (1).

Some years ago Jennings and Scott (9) and Mauguin and Simon (13) reviewed the early studies on the preparation of cyanogen chloride, all of which involved, as do the methods in use today, the reaction of chlorine with hydrocyanic acid or with other cyanides. Jennings and Scott proposed a method using carbon tetrachloride, rather than water, as a diluent to dissipate the heat of reaction; the use of materials such as carbon tetrachloride in this connection has been the subject of patents (3, 6, 14, 18, 19).

A number of synthetic procedures have been described in the literature in addition to those referred to above. A method, first used by Gay-Lussac, involving the chlorination of an aqueous solution of hydrogen cyanide has been further studied (13, 16) and patented (5). Cyanogen chloride has been prepared by the union of gaseous chlorine and hydrogen cyanide (7, 20) and by the electrolysis of an aqueous solution containing hydrochloric acid and either hydrocyanic acid or sodium cyanide (12, 13). Preparations have been reported in which sodium chlorate* or sodium hypochlorite (12) have been used in reaction with an aqueous solution of sodium cyanide and hydrochloric acid.

Held (4) is credited with being the first to suggest the action of chlorine on a solution of zinc sulphate and alkali cyanide as a means of preparing cyanogen chloride. This procedure, which was designed to prevent the formation of paracyanogen, has been regarded unfavourably by certain workers (9, 16), but has been recommended by others (2, 10, 11, 21). The present writers have

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[1] *Manuscript received in original form September 13, 1946, and, as revised, December 9, 1946.*
Contribution from the Chemical Warfare Laboratories, Department of National Defence (Army), Ottawa, and the Department of Chemistry, McMaster University, Hamilton, Ont. The work reported in this paper is largely drawn from N.R.C. reports of restricted circulation, dated March 13, 1943, and February 15, 1944.

[2] *Formerly Captain, Canadian Army. Present address: Canada Packers Ltd., Toronto, Ont.*

[3] *Formerly Graduate Student and holder of a Bursary under the National Research Council of Canada, at McMaster University. Present address: Canadian Industries Ltd., Toronto, Ont.*

[4] *Assistant Professor of Chemistry.*

* *Anon. Pub. Health Repts. 37 : 2744-2747. 1922.*

employed the principle of this method, using the apparatus and procedure described below, to obtain good results.

Apparatus

The reaction flask, *A* (Fig. 1), is a 2 litre round-bottomed flask fitted with an inlet tube, *C*, for chlorine, a thermometer well, a stirrer, and a distillation outlet. Chlorine from a cylinder is passed through concentrated sulphuric acid (20) in the trap *B* (the use of water in this gas flow-rate indicator may lead to the plugging of the chlorine inlet tube in the reaction flask, *A*, by chlorine hydrate) and a glass spiral to absorb vibrational shock, and then is admitted to the reaction flask through the inlet tube, which is fitted at its end with a sealed-in sintered glass disk to distribute the gas immediately below the blades of the agitator. Attached to the shaft of the agitator are two small graphite disks, which bear on larger graphite disks sealed* in the neck of the flask. These graphite disks, carefully machined, were found to provide excellent self-lubricating stirrer bearings. The arrangement may be made essentially gas-proof by keeping the upper bearing covered with water. Violent agitation in the reaction flask is provided by rotating an efficient three-bladed stirrer at 2000 r.p.m.

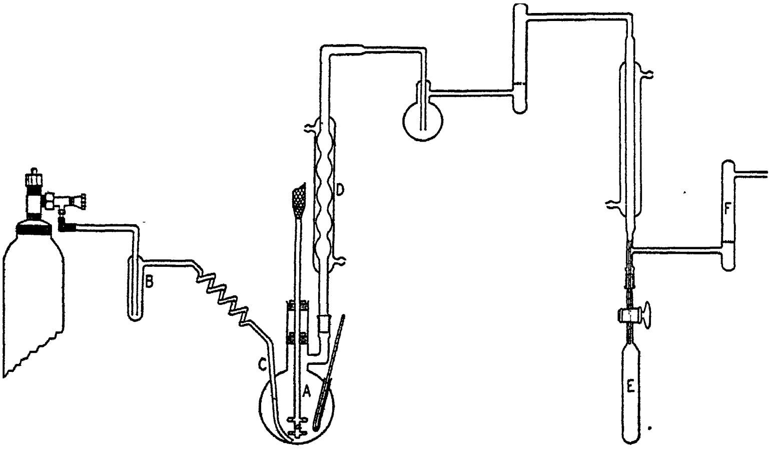

FIG. 1. *Apparatus for the preparation of cyanogen chloride.*

To the distillation outlet of the reaction flask there is connected, by means of a ground glass joint, an Allihn condenser, *D*. The outlet from this foam-breaking condenser leads to a 250 ml. round-bottomed flask, which serves as a foam trap, and thence to two purification and drying tubes (150 by 25 mm.) connected in series. (Only one tube is shown in Fig. 1.) These tubes contain a packing of marble chips and calcium chloride** (12, 16) supported by a sealed-in sintered glass disk. The outlet from the train (to remove acid and water) is sealed to the top of a Liebig condenser, the latter being connected to the receiver, *E*, by means of a ground glass joint. A drip-tip outlet, ring-sealed to the condenser tube, passes through the ground joint and through the 4 mm. bore of a stopcock which is sealed to the ignition tube receiver. This arrangement permits the use of the receiver as a storage container for the cyanogen chloride after distillation, and at the same time eliminates any contact of the liquefied product with the stopcock lubricant. The outlet to the air is fitted with a calcium chloride – soda lime tube, *F*.

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* *'Sauer-eisen', an electrical resistor cement manufactured by the Technical Products Company, Pittsburgh, Penn., was found to be very satisfactory for the glass-to-carbon seals. A mercury seal is unsatisfactory because the attack of chlorine on mercury causes fouling of the seal.*

** *If line blockage occurs owing to caking of the calcium chloride, towers containing marble and activated alumina (indicating type) may be used.*

The reaction flask is clamped in an ethylene glycol – water bath (40% ethylene glycol by volume) contained in a well insulated Pyrex jar. The bath is fitted with a 1000 w. coil heater (encased in a Pyrex shield), a low range alcohol thermometer, and an efficient agitator. Lowering of the bath temperature, when necessary, is effected by the addition of solid carbon dioxide.

The cooling liquid for the condensers consists of an 1 : 1 (by volume) mixture of motor oil (S.A.E. No. 10) and kerosene. It is circulated at the rate of approximately 2 litres per minute by means of a gear-type oil pump, and is cooled by passing it through a glass coil immersed in a dry ice – alcohol mixture contained in a Dewar flask. A T-bore stopcock inserted in the system permits circulation through either the Allihn (foam-breaking) condenser or the Liebig condenser separately, or through both condensers simultaneously. A thermometer is inserted in the circulation system in the return lead between the condensers and the pump. The condensers and all connecting tubing are, wherever possible, lagged with asbestos pulp for thermal insulation. Rubber connections in the circulation system swell appreciably during use; the use of neoprene may be more satisfactory.

Procedure

A solution is prepared by dissolving 147 gm. of sodium cyanide in 300 ml. of water (filtering if necessary) and is added slowly with constant stirring (under a hood) to a solution containing 216 gm. of zinc sulphate heptahydrate in 450 ml. of water.* If necessary a very small additional amount of sodium cyanide is added after the mixing to dissolve any remaining precipitate of zinc cyanide. The resultant solution (which is 4 *M* in sodium cyanide and 1 *M* in zinc sulphate,** or 1 *M* in sodium tetracyanatozincate, $Na_2Zn(CN)_4$, and 1 *M* in sodium sulphate) is filtered and transferred to the reaction flask.

Solid carbon dioxide is added to the ethylene glycol – water bath until the temperature in the reaction flask reaches 5° C. Chlorine at a rate of about

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* *The quantities of reagents specified are sufficient for a theoretical yield of 184 gm. of cyanogen chloride. Using a 6 litre reaction flask, one of the authors (H.W.B.) has a number of times successfully carried out the synthesis on three times as large a scale, using essentially the same apparatus and procedure described in this paper.*

** *Held (4) recommended the use of 1/3 mole of zinc to every 4 moles of cyanide, but later workers (10, 13, 21) have preferred a ratio of 1 mole of zinc to 4 of cyanide. Zappi (21) chlorinated a solution that was 0.77 M in potassium cyanide, and Klemenc and Wagner (10) one that was 1.54 M in potassium cyanide. Mauguin and Simon (13), who used sodium cyanide in place of the potassium salt, employed a number of concentrations of cyanide, including 1 and 2 M.*

200 to 300 bubbles per minute (through 8 mm. tubing) is then admitted to the vigorously agitated reaction mixture, and the addition of dry ice is regulated so that the temperature in the reaction flask is maintained between 0° and 5° C. An appearance of milkiness in the reaction flask indicates the initiation of an exothermic reaction, possibly $Na_2Zn(CN)_4 + 2Cl_2 \rightarrow Zn(CN)_2 + 2NaCl + 2CNCl$ (13). As chlorination proceeds, the mixture becomes more viscous and there appears an increasing amount of white precipitate (presumably zinc cyanide) in the reaction flask, and froth on the surface of the liquid. At this stage the rate of chlorination may be increased provided that the temperature in the reaction flask does not rise above 5° C. (during the last stages of the chlorination it is desirable that the rate be decreased to 200 to 300 bubbles per minute). When the mixture becomes almost a thick paste, the exothermic reaction proceeds with considerable vigour, and it is necessary to cool the bath, which may conveniently be done by the addition of solid carbon dioxide, to approximately −25° C. in order to maintain the temperature within the reaction flask between 0° and 5° C. A thinning of the mixture within the reaction flask due to a decrease in the amount of white precipitate present marks the last stage of the exothermic reaction and the start of an endothermic reaction, possibly $Zn(CN)_2 + 2Cl_2 \rightarrow ZnCl_2 + 2CNCl$ (13). At this stage it may be necessary to turn on the heating unit in the ethylene glycol – water bath to raise the temperature of the bath somewhat in order to maintain the temperature within the reaction flask at 0° to 5° C. As the endothermic reaction proceeds, the mixture progressively becomes thinner, and both the quantity of white precipitate and the foaming of the liquid in the reaction flask decreases. The completion of the reaction is marked by the complete disappearance of the precipitate, and it is very important that chlorination be stopped promptly at this point.

Care must be taken throughout the chlorination procedure that the agitator in the reaction flask is not stopped at any time, otherwise chlorine may escape from the solution and pass over into the scrubbing and condensing system.* Under-chlorination will leave a residue of zinc cyanide in the flask that may cause severe foaming during the distillation. Over-chlorination will result in a product contaminated with chlorine, necessitating a later purification procedure, e.g., distillation from metallic antimony or zinc, fractional distillation under reduced pressure (10), contact with mercury (2, 9, 16) or arsenic (17, pp. 188-191), or with an aqueous suspension of zinc oxide or yellow mercuric oxide (16) or with one of calcium carbonate and zinc oxide at 0° C. (10, 21) followed by drying and distillation.

Distillation of the cyanogen chloride from the reaction mixture is carried out in the following manner. By means of the circulating pump, the kerosene–oil solution is circulated through the Liebig condenser at a temperature of 0° to 3° C. The receiver is maintained at −20° C. by immersing it in a freezing mixture of solid carbon dioxide and alcohol contained in a Dewar flask. The temperature of the ethylene glycol bath is raised slowly by means of the heating unit. When the temperature of the reaction flask reaches 8° to 9° C. the cyanogen chloride begins to distil, and comes over fairly rapidly when the temperature has reached 13° C.

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* *Experience with this synthesis has shown that the rate at which cyanogen chloride is produced may be greatly increased by maintaining a positive pressure of chlorine in the reaction flask during the first stage of the chlorination procedure; this is accomplished by disconnecting the Allihn condenser and blocking the outlet from the flask.*

If foaming occurs and the froth threatens to be carried over into the line, the kerosene–oil solution at 0° to 3° C. is circulated through the foam-breaking condenser. This procedure retards distillation, however, and should be carried out only if necessary. It should be mentioned that the presence of 'Aerosol OT' in the reaction flask decreases the tendency toward foaming.

The distillation is continued by regulating the supply of heat to the reaction flask so that distillation proceeds smoothly at a convenient rate. It is necessary to raise the temperature of the reaction flask to 40° to 45° C. toward the end of the distillation procedure in order to remove the last of the cyanogen chloride from the reaction mixture. When distillation is complete, the receiver is removed from the condenser, the stopcock is closed, and the container is stored in a Dewar flask containing a solid carbon dioxide – alcohol mixture.

If the procedure is carried out properly, a clear colourless liquid, or white solid when frozen, is obtained. The yield was 60 to 70% of the theoretical amount. It has been reported that polymerization of cyanogen chloride to the white solid trimer, cyanuryl chloride, $(CNCl)_3$, is hastened by the presence of moisture (17, pp. 188–191), hydrochloric acid (9, 16, 20), and possibly chlorine (17, pp. 188–191, but cf. 16), but that if the pure material is kept dry and stored in glass, it remains stable for many months (16). The product prepared by the method outlined above showed no evidence of polymerization until it was some months old.

Because of the violently toxic nature* of cyanogen chloride, its synthesis should be carried out under a hood equipped with a fan giving rise to an exceptionally high flow of air. It is recommended that operators of the apparatus wear adequate respirators.

Acknowledgments

The authors are indebted to the Proofing Section of the Chemical Warfare Laboratories and to Messrs. A. S. Tulk and E. T. Clarke of McMaster University for helpful suggestions regarding the construction and operation of the apparatus described.

Acknowledgment is made to the National Research Council of Canada for the financial support accorded and for the award of a Bursary to one of us (R. G. D.).

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* *Cyanogen chloride is a systemic poison and paralyzant (8, pp. 10 and 37); exposure to it in a concentration of 0.4 mgm. per litre for 10 min. is probably lethal (15, p. 175). Its toxicity has been assessed as 13.5 on the basis of chlorine = 1.0 (8, p. 170). In addition to its toxic action, cyanogen chloride is a lachrymator; the concentration required to produce a lachrymatory effect in a few minutes has been given (15, p. 175; 17, pp. 188-191) as 0.0025 mgm. per litre or 1 p.p.m.*

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DIMETHYLDINITROÖXAMIDE[1]

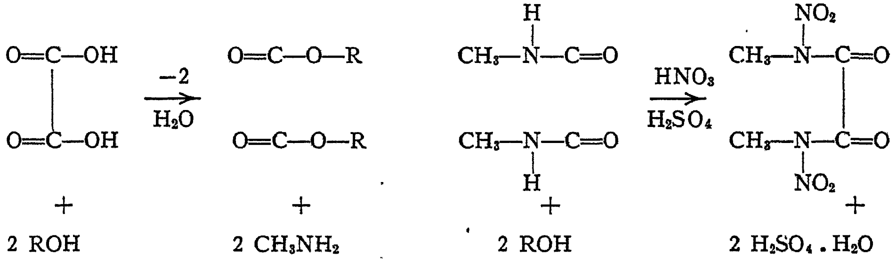
O. C. W. ALLENBY[2] AND GEORGE F. WRIGHT[3]

Abstract

A practical low-cost method is described for the preparation of the explosive dimethyldinitroöxamide. Dimethyloxamide is prepared in 94% yield from an oxalic ester and methylamine, and then is nitrated in 98% yield with slightly more than the requisite amount of nitric acid. The nitrating acid can be recovered safely. The optimum yield is obtained when the waste acid has the composition sulphuric acid monohydrate.

The explosive dimethyldinitroöxamide was first prepared by Franchimont (1, 2, 3) in 93 to 97% yield by treating dimethyloxamide with five times its weight of absolute nitric acid. Thiele and Meyer (6) used rather less nitric acid and supplemented it by addition of sulphuric acid. Their yields of good material were almost theoretical.

In connection with our directive in 1940 to investigate practical methods of nitramine explosive manufacture, we sought the most economical method for preparing dimethyldinitroöxamide. The following formulation



$$\mathrm{(COOH)_2 + 2\,ROH \xrightarrow[H_2O]{-2} (COOR)_2 + 2\,CH_3NH_2 \qquad (CONHCH_3)_2 + 2\,ROH \xrightarrow[H_2SO_4]{HNO_3} [CON(NO_2)CH_3]_2 + 2\,H_2SO_4 . H_2O}$$

indicates these economies must be applied firstly to dimethyloxamide formation, and secondly to its nitration.

Dimethyloxamide has been prepared from ethyl oxalate and methylamines (8, pp. 50-51) or a mixture of methylamines (9, 10, pp. 443-464) but we chose instead to use amyl oxalate, because this ester can be prepared simply by azeotropic distillation of oxalic acid and the alcohol (7, pp. 337-339). For example, we obtained an 85% yield of amyl oxalate in three hours by withdrawing the water from a decanter as fast as it co-distilled with the amyl alcohol which returned to the reaction vessel.

This amyl oxalate is then added slowly to carbon tetrachloride previously saturated with methylamine and maintained in saturation during the addition. The yield of dimethyloxamide of nitration grade constitutes 94% of the theoretical.

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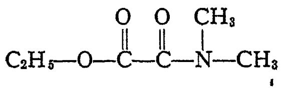
Contribution from the Chemical Laboratory, University of Toronto, Toronto, Ont.

[2] *Graduate Student.*

[3] *Professor of Chemistry.*

Pure monomethylamine is not easily available, but an ordinary methanol–ammonia reactor yields, after ammonia is stripped off, a mixture of 88.6% monomethylamine, 6.86% dimethylamine, and 4.78% trimethylamine together with methanol. When the mixture was used to replace the pure monomethylamine in the above procedure, an unsatisfactory product was obtained, which probably contained ethyl dimethyloxadamate. This oily substance



$$C_2H_5{-}O{-}\overset{O}{\overset{\|}{C}}{-}\overset{O}{\overset{\|}{C}}{-}\overset{CH_3}{\overset{|}{N}}{-}CH_3$$

was found by Hofmann (4, 5) to be the contaminant when he attempted a similar preparation with mixed amines.

This impurity was eliminated simply by adding the amyl oxalate to a large excess of the methylamines, which also acted as the reaction medium. Because of its preponderance, the monomethylamine reacted by preference; and the large amine excess precluded any half-ammonation which might yield products like ethyl dimethyloxamadate. When the reaction was complete, the excess amines were distilled off and the residue washed with carbon tetrachloride to remove amyl alcohol (which should be returned to the esterification reaction). The yield of dimethyloxamide by this method is 86% of theoretical and its melting point, 214° to 215° C., indicates it to be entirely suitable for nitration. The material will, however, be unsuitable for nitration if oxidizable amyl alcohol is not entirely washed out, or if the original amine mixture contains more than 2 to 3% of ammonia. It is not difficult, however, to ensure an amine mixture free from ammonia because of the differences in properties. Thus the solubility of methylamine in carbon tetrachloride at 25° C. is 1.1%, while that of ammonia is 0.003%. Such a differential cannot be used directly, since the presence of methanol vitiates this favourable ratio, but it serves to show that purification systems to remove ammonia can easily be devised.

The nitration method of Thiele and Meyer is clearly not the ideal practical procedure, firstly because it is wasteful of nitric acid, and secondly because the acid mixing is carried out with the dimethyloxamide in solution. This would invite decomposition unless heat removal were extremely efficient.

We found that a 98% yield of dimethyldinitroöxamide could be produced using slightly more than the theoretical quantity of nitric acid in a mixed acid prepared from 60% nitric acid and 20% oleum. The mixed acid required for one mole of dimethyloxamide contains 2.1 moles of 100% nitric acid, 5.51 moles of 100% sulphuric acid, and 3.15 moles of water. Upon completion of nitration, the remaining acid will therefore be almost exactly sulphuric acid monohydrate. This condition is necessary for attainment of maximum yield. It may be seen from Fig. 1 that the yield falls sharply when the water content of the mixed acid deviates slightly from the optimum. It is fortunate that the optimum acid mixture is the cheapest that can be prepared from common ingredients.

The crude explosive is pure according to melting point criteria, but we usually crystallized it from carbon tetrachloride containing a little calcium carbonate in order to ensure freedom from acid and water, and also to deposit on it a trace of paraffin in order to make it water repellant. This may be advisable because of its tendency toward hydrolysis by water. Fig. 2 shows that the rate of this hydrolysis depends on the amount of water present; in

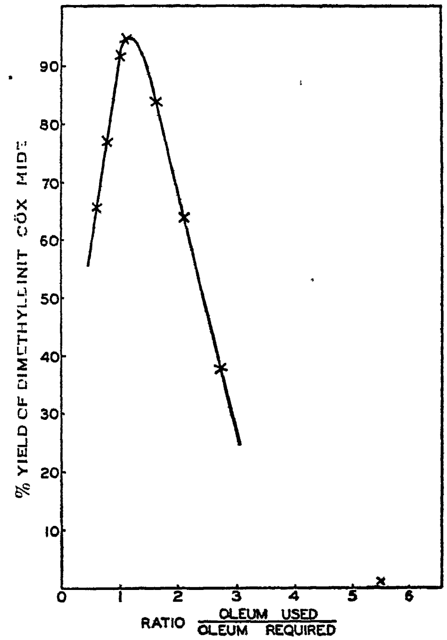


FIG. 1. *Nitration of dimethyloxamide.*

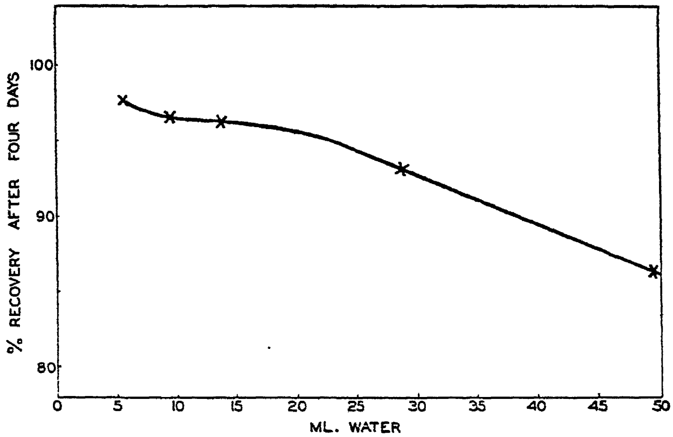


FIG. 2. *Hydrolysis of dimethyldintiroöxamide.*

other words the substance is stabilized by its own decomposition products. The explosive is non-hygroscopic, and destruction by water hydrolysis ought not be more severe than with the common explosive nitroguanidine, which has similar properties.

Dimethyldinitroöxamide cannot be used as a pourable explosive since it decomposes at its melting point of 124° C. Its power as measured in the ballistic mortar and Trauzl block is 1.05 times that of T.N.T. The impact sensitiveness of the pure explosive is equivalent to that of T.N.T.; a film coating (less than 0.1%) of paraffin reduces this sensitiveness to 0.9 that of T.N.T. It is, however, more sensitive than T.N.T. to sympathetic detonation from 60% dynamite. The rate of detonation of dimethyldinitroöxamide is 4900 to 6760 m. per sec., depending on the density of 1.03 to 1.42. Its heat of formation is 74.5 kcal. per mole, based on a heat combustion of −508.4 kcal. per mole. It forms a pourable mixture with setting point 75° C. when mixed in equimolar amount with picric acid. The rate of detonation of this mixture is 6680 to 7500 m. per sec., depending on densities of 1.41 to 1.59.

Experimental*

Dimethyloxamide from Pure Methylamine

A 12 gal. stainless steel vessel was equipped with a wide-sweep stirrer, internal cooling coil, and external spray water cooling. Into this vessel was introduced 3.2 U.S. gal. of carbon tetrachloride which was saturated with methylamine by means of a gas inlet at the bottom. By means of stirring and cooling, the temperature was held at 20° C. while 12.8 lb. of dibutyl oxalate (used interchangeably with the amyl ester) and 4.05 lb. of methylamine were added over a four hour period. After one hour's subsequent stirring, the slurry was centrifuged and washed with one gallon of carbon tetrachloride. The yield of 7 lb. of nitration-grade dimethyloxamide (m.p. 210° to 211° C.) was 94% of theoretical on the ester basis.

Dimethyloxamide from Mixed Methylamines

A mixture of the amines and methanol in the proportions 1210 gm. (39.4 moles) of methylamine, 93.5 gm. (2.08 moles) of dimethylamine, 66.5 gm. (1.13 moles) of trimethylamine, and 285 gm. (9.2 moles) of methanol was condensed into a flask cooled to −15° C. and equipped with dropping funnel, stirrer and reflux condenser cooled to −30° C. To this stirred liquid was added, over 25 min., 230 gm. (1 mole) of diamyl oxalate. After several hours, the mixture of amines was allowed to distil off, and the residue washed on a filter with five 300 cc. portions of carbon tetrachloride. The yield of dimethyloxamide melting at 214° to 215° C. was 101 gm. or 86% of the theoretical amount. A further 6.2 gm. of material unsuitable for nitration was obtained from the wash liquors.

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* *All melting points are corrected against known standards.*

It is obvious that the latter procedure can be adapted to the use of pure methylamine, although the first procedure cannot be used with mixed amines.

Nitration of Dimethyloxamide

A mixture of 12.6 lb. (68 moles) of 75% nitric acid and 39 lb. (176.8 moles) of 98% sulphuric acid (or its equivalent in 58% nitric acid and 20% oleum) was mixed carefully to ensure a low nitrous acid content and then cooled and maintained at 30° C. in a 12 gal. stainless steel kettle equipped with external spray cooling and a stainless steel stirrer with four staggered blades 4 by 6 in. which cleared the kettle wall (13 in. diameter) by only ½ in. This stirrer was driven by reduction gear at 100 to 120 r.p.m. while 8.63 lb. (33.7 moles) of dimethyloxamide was added over one hour. The heavy slurry was stirred two hours longer; the mixture will evolve gas if the temperature rises much above 30° C.

The slurry was filtered without difficulty through glass cloth. The precipitate was then transferred portionwise into 6 U.S. gal. of stirred cold water, refiltered and washed with 10 U.S. gal. of water until neutral to bromcresol green. This product was air-dried to weigh 15 lb. (98% of theoretical on dimethyloxamide basis) and melt at 124° C.

The spent-acid filtrate, consisting of sulphuric acid monohydrate with the 5% nitric acid excess, usually warmed up during filtration, unless it was cooled, and evolved some nitrogen oxides. Dilution of this liquor with twice its volume of water precipitated 1.9% of the theoretical yield of dimethyldinitroöxamide (therefore the remainder of a 100% yield) as a tan powder, m.p. 122° to 124° C.

In practice this small amount of material would probably be sacrificed by heating the undiluted liquor. A smooth easily regulated fume-off of nitrogen oxides thus occurs, leaving the sulphuric acid free from explosive and nitric acid and thus clean enough for subsequent concentration or fortification. This denitrated sulphuric acid does however contain a small amount of nonexplosive organic material.

Crystallization of Dimethyldinitroöxamide

When 15.8 lb. of air-dried explosive was dissolved in 12.6 U.S. gal. of boiling carbon tetrachloride containing 5 gm. of suspended calcium carbonate, a 91% recovery was obtained by cooling. The melting point of 124° C. was not raised by this crystallization, which was probably unnecessary in view of the purity of the crude material. However, the 1.5 lb. of material recovered by evaporating the solution medium melted at 123.5° to 124° C. The addition of 0.16 lb. of paraffin to the hot carbon tetrachloride caused a more rapid crystallization which began after slight cooling below the boiling point and thus tended to clog the hot filter unless it was adequately heated. The resulting crystals were strongly water repellant, but the bulk density was decreased from 0.8 to about 0.6.

Hydrolysis and Thermal Stability of Dimethyldinitroöxamide

The data recorded in Fig. 2 were obtained by shaking 5-gm. portions suspended in various amounts of distilled water in air-tight tubes at 25° C. for four days. They indicate, by extrapolation toward minute amounts of water, that hydrolysis due to dampness would be negligible. A sample of dry material at 70° C. for three weeks in a closed tube showed no decrease in melting point and no volatile acidity to bromcresol green or congo red papers. No evolution of nitrogen oxides from the dry explosive is detectable after four hours at 100° C.

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OSMOTIC PRESSURE MEASUREMENT AND THE INSTABILITY OF HIGH POLYMERS[1]

By A. F. Sirianni,[2] L. M. Wise,[2] and R. L. McIntosh[3]

Abstract

In attempting to obtain accurate osmotic data in the low concentration range, it was found that the results were influenced by the diffusion of solvent from the cell through the membrane gasket. This behaviour was prevented by auxiliary sealing in a cell of new design, and results obtained with the improved cell are compared with those obtained with previous types of osmometer. A partial re-examination of the influence of preparation of the membrane was made in order to check results reported by Robertson, McIntosh, and Grummitt, and the different behaviour of caustic swollen and water swollen cellophane membranes has been confirmed, although quantitative agreement for water swollen membranes between the two investigations was not obtained. Using caustic treated membranes the molecular weight of a polyvinyl acetate sample was found to be the same within experimental error in three solvents.

Further results on the changes in intrinsic viscosity and molecular weight brought about by ageing at elevated temperatures in the presence and absence of oxygen are reported for polyvinyl acetate and polymethyl methacrylate. It appears that oxygen is necessary to bring about molecular weight changes, and the degradation is due to scission of the chains at weak points. The evidence also suggests that changes in molecular shape may occur, since intrinsic viscosity values altered in some cases without evidence of molecular weight variation. This last observation is apparently outside the limits of error in reproducing osmotic pressure values.

Part I

Osmometry

INTRODUCTION

It has been known for some time that solutions of high polymers are not entirely stable when stored over long periods of time. Several instances of instability in solutions of high polymers are recorded in the literature. Mead and Fuoss (23) reported changes in viscosity of solutions of polyvinyl chloride in methyl amyl ketone and cyclohexanone. Wehr (34) states that the stability of solutions of polyvinyl chloride in several solvents depends on the degree of saturation of the polymer, the light intensity, and the presence of catalysts. Blaikie and Crozier (4) found that solutions of polyvinyl acetate in glacial acetic acid at 160° C. initially decreased in viscosity and then increased. Decreases in viscosity on standing have also been noted by Jirginson (16) for solutions of gelatin in water, by Bartell and Cowling (2) for alkali cellulose and by Ott (30, Chap. VIII) for pure cellulose. In many cases (2; 4; 30, Chap. VIII) it has been noted that the presence of oxygen

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[2] *Graduate student, at the time holder of a Studentship under the National Research Council of Canada. Present address: National Research Council, Ottawa, Canada.*

[3] *Chemist, National Research Council, Ottawa, Canada.*

affects the degradation. Naunton (29) showed that rubber solutions exposed to light and oxygen slowly absorbed oxygen, while the viscosity of the solution decreased.

An investigation of the instability of solutions of polyvinyl acetate, polystyrene, and polymethyl methacrylate in three solvents, bis(2-chloroethyl) ether, nitrobenzene, and bis(2-chloroethyl) sulphide by Morrison, Holmes, and McIntosh (26) showed that viscosity changes were dependent on the presence of impurities, such as oxygen and ferric salts.

However, on account of the theoretical limitations of the viscosity method, it was impossible to decide definitely whether the viscosity changes were due to changes in the molecular weight of the polymer or to variation in such other factors as (*a*) the degree of solvation of the polymer, (*b*) the orientation or configuration of the macromolecules in solution, (*c*) the chemical nature of the polymer. Osmotic measurements, which theoretically furnish more absolute data, were therefore determined on some of the aged samples (21) and showed that a definite molecular weight change did take place.

The present work was undertaken as a continuation of the studies on the ageing of polymers under varying conditions. During this work, difficulties in osmotic practice came to light. Attempts were made to correct these inadequacies. It is probable that the difficulties discovered were present undetected in the apparatus of other workers, and their probable influence on the results of other workers has therefore been investigated in a preliminary manner.

Towards the beginning of this work, Robertson, McIntosh, and Grummitt (32) showed that, for the system polyvinyl acetate in acetone, osmotic pressures determined using swollen cellophane membranes, prepared by the method of Carter and Record (6), and using cellophane membranes that had been treated with sodium hydroxide, yielded different results. These differences are not explicable as due to imperfectly semipermeable membranes. There is evidence in the literature that this behaviour is a specific case of a more general phenomenon. Fuoss and Mead (9) suggest that a membrane is not suitable unless it is swollen by the solvent employed. Such an explanation is not far different from the explanation proposed by Robertson, McIntosh, and Grummitt (32), which presumes that adsorption of polymer at the membrane is prevented by preferential adsorption of solvent.

Unfortunately, the dynamic osmometer used by Robertson *et al.* could not be used for very low osmotic pressures and, consequently, required a long extrapolation to infinite dilution for the curve osmotic pressure/concentration versus concentration (i.e., π/C vs. C). It was therefore impossible to determine definitely whether the π/C versus C curves for the two types of membranes yielded identical intercepts and thus identical values for the molecular weight. This question was therefore reinvestigated using a modified type of osmometer. At the same time, several other points of fundamental interest have been reinvestigated.

The work reported here is therefore broadly divided into two parts, the first describing the construction of the osmometer and the investigation of membrane preparation and other fundamental points, and the second dealing with the results obtained in the continuation of the investigations on the ageing of polymers.

Experimental

The Osmometer

In designing a suitable osmometer, several factors must be considered:

(1) There must be no interaction between the materials of the osmometer and the solvents or polymers used.

(2) It must be free from leaks.

(3) The presence of bubbles should be easily recognizable and the bubbles easily removable.

(4) The membrane should be held in place as rigidly as possible, since the apparent rate of approach to equilibrium depends on the rigidity of the membrane (7).

(5) On account of the high molecular weights of the polymers and the consequently low osmotic pressures to be measured, a high degree of accuracy is required. Since the π/C versus C curve must be extrapolated to infinite dilution, determinations must be possible on very dilute solutions.

(6) The osmometer should be as rapid in operation as possible.

Osmometers generally may be divided into two classes, dynamic and static. In the dynamic type (5, 33) the flow of solvent across the membrane toward the solution side is opposed by an externally applied pressure, and that pressure determined which just stops the flow of solvent. In the static method (7) the height of liquid set up in a vertical capillary on the solution side is measured. The dynamic type of osmometer, used by Robertson, McIntosh, and Grummitt (32) and by McIntosh and Morrison (21), proved tedious in operation and required a long extrapolation to infinite dilution.

The osmometer originally constructed in the present work was based on the combined static and dynamic osmometer designed by Montonna and Jilk (25), Fuoss and Mead (9), and Flory (7). It consisted of two metal plates, each containing a shallow well surrounded by a flat ring $3\frac{3}{4}$ in. outside diameter. The well contained a series of concentric ridges to support the membrane. The two plates were bolted together over the membrane, which was thus presumed to behave as a gasket, between the flat rings, to seal the osmometer. Each well led to a vertical capillary of 0.5 mm. bore, in contrast to previous designs in which one well led to a capillary tube and the other to a wide tube.

Such an osmometer proved unsatisfactory. The levels in both capillaries dropped simultaneously, irrespective of the external pressure of the thermostating liquid, indicating the presence of a leak. Intensive investigation of several modifications showed that the membrane does not form a satisfactory gasket. Carter and Record (6) arrived at a similar conclusion and Flory (7) states that his cell may have been leaking, but does not locate the leak at the sealing face. Fuoss and Mead (9) state that, with solvent in both compartments of the osmometer, a difference of at least 1 mm. is observed between the capillary levels. Lossing (18) reports a similar 'asymmetry', whose magnitude can be altered by tightening the bolts about the cell. Nevertheless, the observation of leakage is in contradication to most of the recent literature (3, 7,10). It is therefore proposed to present in some detail the experimental evidence.

The criterion of the existence of leakage lay in whether the liquid levels in the capillaries of a thermostatically controlled cell remained constant over a period of several hours. Conventional tests, such as immersing the osmometer in water and applying air pressures up to 30 lb. per sq. in., proved inadequate, since an osmometer, while appearing free from leaks by this test, still leaked when filled with solvent. The leak was definitely located at the membrane by replacing the membrane with a sheet of 'Composition' metal foil (Pb 97.5%, Sn 0.5%, Sb 2%) of about the same thickness and compressibility as the membrane. The liquid levels remained constant over a period of six hours, except for a drop of 0.015 cm. per hr. from evaporation from the capillaries. Nevertheless, when the metal foil was replaced with a cellophane membrane the usual drop in the levels of 0.2 to 0.6 cm. per hr. was observed. A perfect imprint of the sealing face was invariably found on the membrane. Furthermore, membranes of denitrated collodion, much thicker than cellophane membranes, gave still more rapid leakage when installed in the osmometer. It therefore appears that no mechanical leak existed, but that diffusion took place directly through the membrane.

While several methods of preventing the leakage are undoubtedly feasible, only the one will be described that was adopted, because it gave greatest satisfaction and involved the least alteration of the general design.

On one half-cell, the sealing ring was lowered 0.01 in. below the tops of the ridges in order to accommodate a gasket of 'Composition' metal foil. At the outer edge of the ring on one half-cell was machined a second ring $\frac{1}{8}$ in. wide and raised 0.007 in. above the first ring. This second ring exactly matched a groove in the sealing face of the other half-cell $\frac{1}{8}$ in. wide and 0.007 in. deep (Fig. 1). In practice the membrane fitted inside the ridge and groove system, while a layer of 'Composition' foil 0.01 in. thick was placed over the whole sealing face and sealed at the ridge and groove. The two half-cells were clamped together by means of eight $\frac{3}{16}$ in. bolts around the edge of the cell.

The wells to contain solvent and solution were constructed as described by Robertson, McIntosh, and Grummitt (32), with drill holes leading to the bottom for filling and draining purposes. The tops of these drill holes were initially closed by means of needle valves, consisting of tapered steel plugs fitting into brass cones, tapered at a slightly different angle. Such a system could not be made consistently leak proof. The steel plugs were therefore coated with solder, which was machined to approximately the same taper as the plug. This soft tip gave a vacuum tight seal. The capillaries (0.5

mm. ± 1%) were connected to the wells through Fernico bushings (9). Evaporation from the ends of the capillaries was decreased to 0.015 cm. per hr. by leading the ends over thermostatically controlled bulbs of solvent. It was not possible to eliminate evaporation completely.

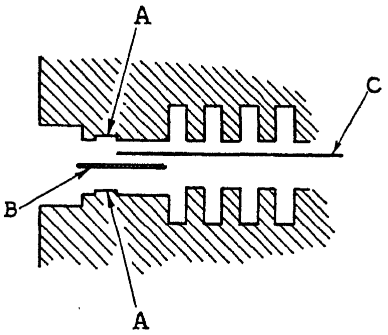

FIG. 1. *Sealing system. A. Ridge and groove system. B. 'Composition' foil. C. Membrane.*

A photograph of a slightly modified form of this osmometer is shown in Fig. 2. It differs only in being provided with a flooding ridge to facilitate the installation of membranes.

The assembly of the cell required great care to prevent drying and consequent loss of permeability of the membrane. When a flooding ridge was present, the membrane could be kept under solvent in the well formed by the ridge while the cell was being assembled. If the solvent was dense enough to float the membrane, or if no flooding ridge was present, the attention of two persons was required. One half-cell, with the metal gasket, was placed on a slightly inclined support. The membrane was installed while being thoroughly flooded with solvent, the second half-cell put in place, and flooding continued through the filling tubes while the system was being bolted.

Bubbles were partially removed by filling the chambers to just above the membrane and oscillating the cell. Final adjustment of liquid levels was made through the capillaries with a fine pipette. In spite of the utmost care, bubbles frequently manifested themselves after the osmometer was in use, either by actual appearance, or by causing a continuous movement of the liquid levels in excess of that from evaporation. Gee (10) and Flory (7) attributed bubbles to trapped air which could be removed by oscillation. Present observations indicate that this is not entirely the case. Bubbles rarely appeared until the temperature of the cell was raised somewhat by placing it in the thermostat. Furthermore, bubble formation was much more pronounced when a fresh membrane was placed in the osmometer. The difficulty caused by bubbles became progressively worse over a period of months, probably as a result of corrosion, since either remachining the metal or gold plating it reduced markedly the difficulty from bubbles (22). The extent of the difficulty also varied with the solvent used, increasing in the order benzene, chloroform, acetone.

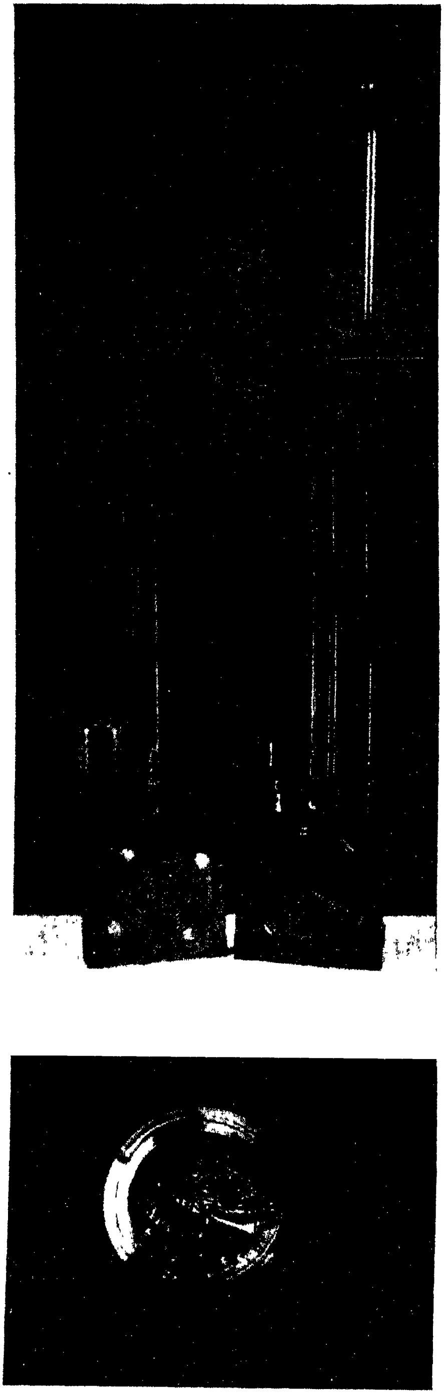

FIG. 2. *Gold plated osmometer. Above—Osmometer. Below—'Composition' foil, membrane and solder-tipped valve plug.*

It appears, therefore, that bubbles, in addition to trapped air, arise from air dissolved in the solvent and adsorbed on the membrane and cell faces. The emergence of this air is probably aided by increased temperature, and the removal of bubbles hindered by rough surfaces such as arise from corrosion of the metal.

In a gold plated osmometer, bubbles were removed by oscillation of the cell during filling and by applying gentle suction at the ends of the capillaries to remove those that subsequently appeared. For unplated osmometers, it was found advisable to warm the filled osmometer for several hours at a temperature 2° to 3° C. higher than the thermostat temperature and then, with the valves open, to oscillate the liquid levels. In all cases, bubble effects were considered absent when the movement of the liquid levels had decreased to that attributable to evaporation (0.015 cm. per hr.).

The osmometer was thermostated at 30 ± 0.001° C. in an oil-bath controlled by a mercury thermoregulator, equipped with a supersensitive relay and a vibrator.

It was found more convenient to use the system as a static rather than a dynamic osmometer.

Careful machining of the plates was required in order that the membrane might be held rigidly. A loosely held membrane had a low apparent permeability.

Membranes

For investigation of the effect of caustic on cellophane membranes (32), both caustic treated and untreated membranes were prepared. For untreated membranes, squares of cellophane No. 600 PT, obtained from Canadian Industries Limited, were first partially freed of plasticizer by being boiled in water for one hour. Circles of the required size were then cut out, allowing $\frac{1}{8}$ in. in diameter for subsequent shrinkage. Final traces of plasticizer were removed by a second boiling in water (19). In order to accommodate the membrane to the solvent the membrane was dipped twice for two minutes in 95% ethanol, stored in 99% ethanol for 12 hr. and then transferred to anhydrous acetone.

For caustic treated membranes, after removal of plasticizer, the membranes were soaked in 2% sodium hydroxide solution for 15 min. In order to accommodate the membrane to the solvent without washing out the caustic, the membranes were dipped for two minutes in distilled water and twice, for two minutes each, in 95% ethanol. They were then placed in 99% ethanol for 15 min. and stored in anhydrous acetone. When a brass osmometer was used with acetone as solvent, it was found that a large downward drift in the liquid levels occurred if more than 2.3 mgm. of sodium hydroxide was contained in the membrane. No such effect was observed for benzene or chloroform, nor for acetone in a gold plated cell.

Intrinsic Viscosities

Intrinsic viscosities were measured at 20 ± 0.02° C. in the ordinary manner by means of an Ostwald type viscometer having outflow times of approximately 72, 76, and 136 sec. for chloroform, acetone, and benzene, respectively.

Materials

The polyvinyl acetate was a commercial product (Gelva V 45 and V 360) supplied by Shawinigan Chemicals Ltd. It was purified by being dissolved in acetone, filtered, precipitated into distilled water, and dried *in vacuo.*

The polymethyl methacrylates were supplied by E. I. duPont de Nemours and Co. (NDR 474, 471, 359). They were dissolved in benzene, filtered, and precipitated into petroleum ether.

The chloroform and acetone were Merck Reagent Grade. They were dried over calcium chloride, distilled, and stored over Drierite. The benzene was Mallinckrodt's Reagent Grade, dried over calcium chloride and stored over sodium wire. The ethanol was Standard Chemical Co. 95%, and the petroleum ether was Mallinckrodt's Reagent Grade, b.p. 30° to 60° C.

Preparation of Solutions and Test for Semipermeability

Solutions were made up by weight. For determination of the tiny quantities occasionally appearing on the solvent side during tests for semipermeability of the membranes, the liquid was run into distilled water and the resultant turbidity estimated with a Fisher A.C. Model Electrophotometer. Where the solvent was immiscible with water, the solvent was evaporated on a steam-bath and the residue taken up with acetone before being mixed with the water. Concentrations as low as 0.001 gm. per 100 cc. could be detected.

RESULTS

Comparison of Osmometers

Since the difficulties encountered in designing a suitable osmometer were such as to make it probable that they were present in osmometers used by other workers, a comparison was made between osmotic pressures determined with the metal-gasketed and with the old types of osmometer. Solutions of Gelva V 45 and V 360 were used with membranes of comparatively low caustic content. The results are shown in Fig. 3. Curves 1 represent determinations with the present, improved osmometer. Curves 2 were determined by Robertson, McIntosh, and Grummitt (32) on identically prepared polymer samples, using a dynamic osmometer with a membrane gasket. Curve 3 was established with the present osmometer without the 'Composition' foil gasket, under the apparently unwarranted hypothesis that the rate of leak was identical on both sides and would not affect the osmotic pressure. The leak (about 0.1 cm. per hr.) masked the presence of bubbles on the solution side, so that most of the results are high. Finally, the capillary on the solvent side was replaced with a large tube to give a true Fuoss and Mead type of osmometer (9). The masking effect of the large tube permitted both bubbles and leakage to remain undetected. The bubble effect presumably predominated, resulting in the points, shown as triangles, being high, rather than low.

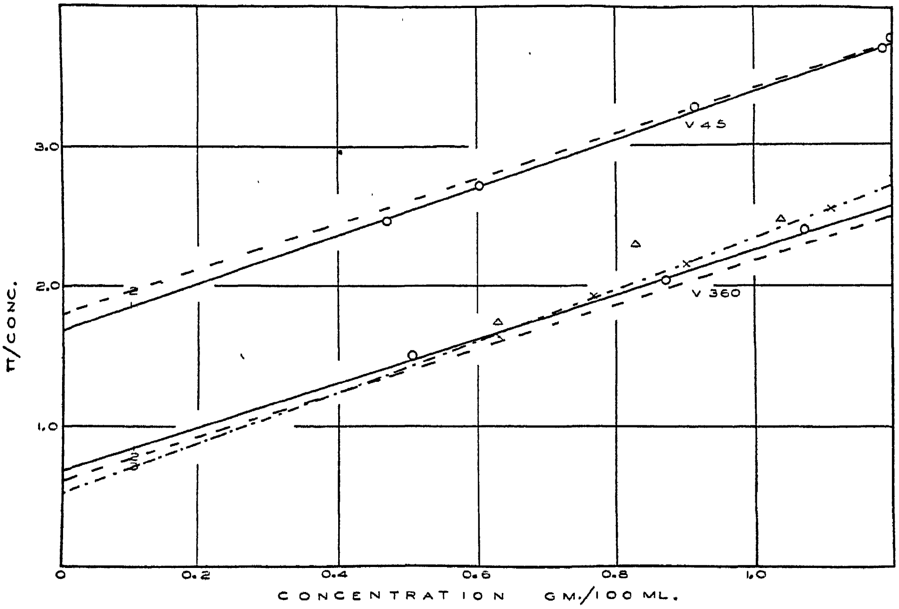

FIG. 3. *Data obtained with improved and conventional type osmometers.*
Curve 1: ————————
Curve 2: — — — — —
Curve 3: — · — · — · — ·

Molecular Weights in Different Solvents

Published osmotic data (11) indicate that the π/C versus C curves for a given polymer in different solvents may have different slopes but identical intercepts and thus yield identical values for the molecular weight. The point is of such fundamental importance that it was reinvestigated with the improved osmometer. The molecular weight of Gelva V 45 in acetone, benzene, and chloroform was determined using a 2% caustic treated membrane. As seen in Table I and Fig. 4, the intercepts, and so the molecular weights, are identical

TABLE I

MOLECULAR WEIGHT OF POLYVINYL ACETATE (GELVA V 45) IN VARIOUS SOLVENTS

Solvent	$\left(\frac{\pi}{C_2} - \frac{RTd_1}{3M_1d_2^3}C_2^2\right)_{C_2=0}$	$M_n \times 10^5$	Slope	μ_1
Chloroform	1.87	1.38	3.32	0.377
Benzene	1.84	1.40	1.52	0.427
Acetone	1.82	1.41	1.50	0.439

within 1.5%. It is noteworthy that, in these curves, the negative term $\frac{RTd_1}{3M_1d_2^3} C_2^2$ in Huggins' equation (14) is not negligible and has been included in the calculations. Furthermore, the curves for benzene and acetone are almost identical, while that for chloroform differs markedly in slope. This is reflected in the values of the Huggins' characteristic constant, μ_1 (13).

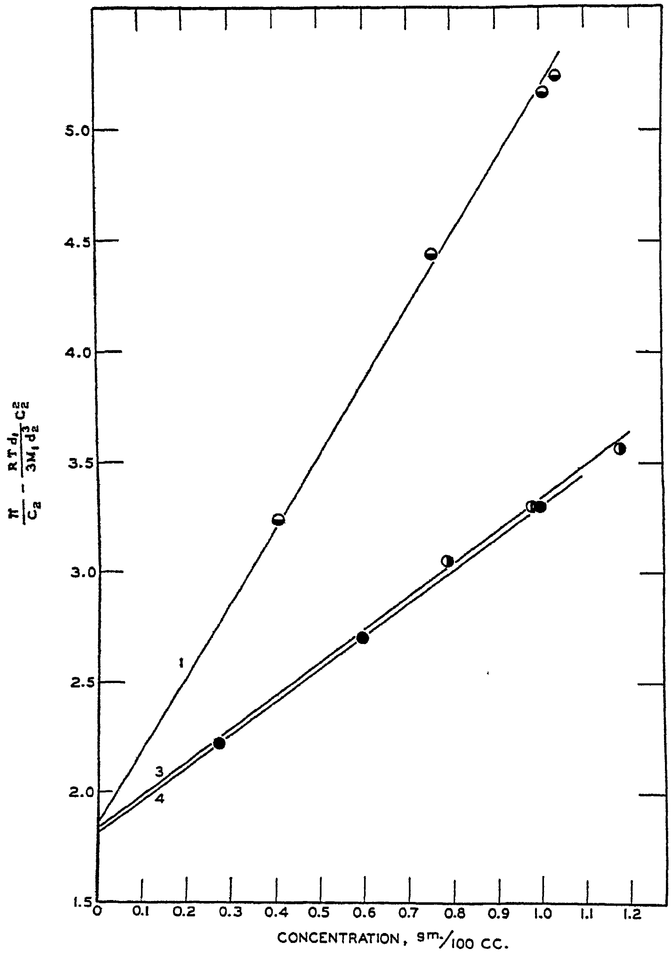

FIG. 4. *Osmotic pressure of Gelva V 45 in different solvents. 1. Chloroform. 3. Benzene. 4. Acetone.*

For comparison, intrinsic viscosities were determined for the same systems. The results are shown in Table II and Fig. 5.

As in the case of the osmotic pressures (Table I), the curves in benzene and acetone are almost identical, while that in chloroform differs markedly. In spite of the marked difference between the curve for chloroform and the other

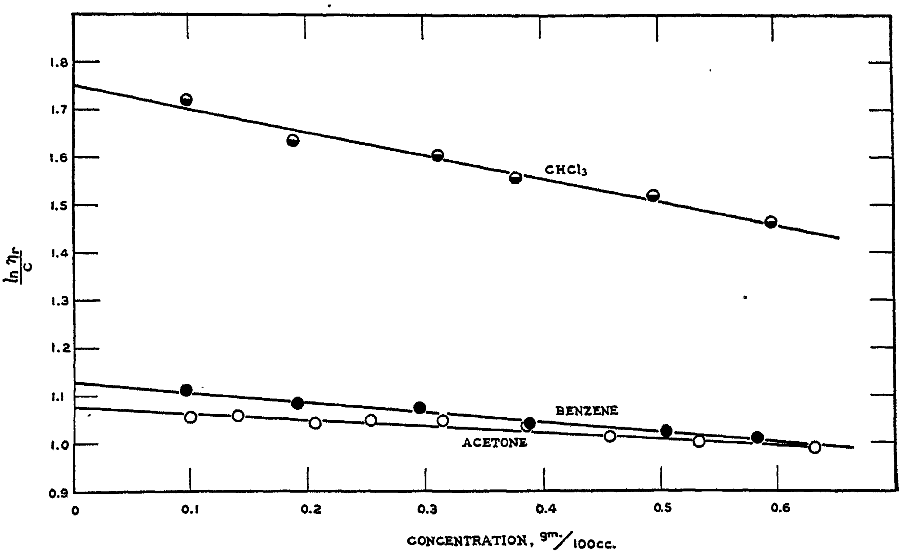

FIG. 5. *Viscosity of Gelva V 45 in different solvents.*

TABLE II

VISCOSITY AT 20° C. OF POLYVINYL ACETATE (GELVA V 45) IN VARIOUS SOLVENTS

Solvent	$[\eta]$	k'
Chloroform	1.75	0.34
Benzene	1.12	0.35
Acetone	1.08	0.38

two, presumably a result of differences in solvent–solute interaction, Huggins' characteristic constant, k' (14), is almost unchanged.

Osmotic Pressures with Different Membranes

As previously stated, Robertson, McIntosh, and Grummitt (32) found that, for polyvinyl acetate in acetone, swollen cellophane membranes prepared by the method of Carter and Record (6) gave a different π/C versus C curve from that obtained when the membrane was treated with sodium hydroxide. This was explained as due to adsorption of polymer on the Carter and Record membranes. Since the dynamic osmometer of Robertson, McIntosh, and Grummitt was not sufficiently accurate to permit the point to be decided definitely, it was reinvestigated for Gelva V 45 in acetone, using the metal-gasketed osmometer. For the Carter–Record membranes, determinations were made on successive fillings until the osmotic pressure became constant. The results are shown in Table III and Fig. 6.

Robertson, McIntosh, and Grummitt (32) state that no appreciable adsorption takes place on membranes that have been treated with caustic.

TABLE III

OSMOTIC PRESSURES OF POLYVINYL ACETATE IN ACETONE WITH DIFFERENT MEMBRANES

Conc., gm./100 cc.	Filling	π (gm./cm.^{2})	$\frac{\pi}{C_2}$	$\frac{\pi}{C_2} - \frac{RTd_1}{3M_1d_2^3}C_2^2$
Carter–Record membranes				
0.414	1	0.830	2.00	
	2	0.940	2.27	
	3	0.994	2.39	
	4	0.970	2.35	2.36
0.628	1	1.659	2.64	
	2	1.699	2.70	
	3	1.705	2.71	2.68
1.01	1	3.36	3.34	
	2	3.37	3.35	
	3	3.37	3.35	3.28
1.22	1	4.50	3.69	
	2	4.55	3.73	
	3	4.61	3.77	3.67
(0.0)		—	1.63	1.67
2% Caustic treated membrane				
0.594	—	1.61	2.71	2.69
0.997	—	3.35	3.36	3.29
0.270	—	0.602	2.23	2.22
0.0	—	—	1.80	1.82

In the present work, at low pressures, sufficient adsorption took place to decrease the osmotic pressure by 2 to 3%. At the higher pressures, at which Robertson *et al.* worked, no adsorption was detected. Since the extent of adsorption was itself not of particular interest for caustic treated membranes, accommodation of the membranes with solution for at least six hours was adopted as standard practice before the final filling was made.

Adsorption by Carter–Record type membranes was higher than for caustic treated membranes. The decrease in osmotic pressure on this account varied from 0.3 to 14.4%. This is less than that observed by Robertson, McIntosh, and Grummitt (32). However, the membranes in the present work were highly swollen, and Robertson (31) notes qualitatively that adsorption effects with fully swollen membranes are less pronounced.

In contrast with the results of Robertson *et al.*, the curve for the caustic treated membrane is above that for the untreated one. However, the present work shows definitely that the intercepts for the two curves are different.

At present it is not possible to state whether the differences between the results of Robertson, McIntosh, and Grummitt and the present work are due to the nature of the Carter–Record membranes employed in the two cases or whether the effect is due to the improved sealing at the membrane face in the present work.

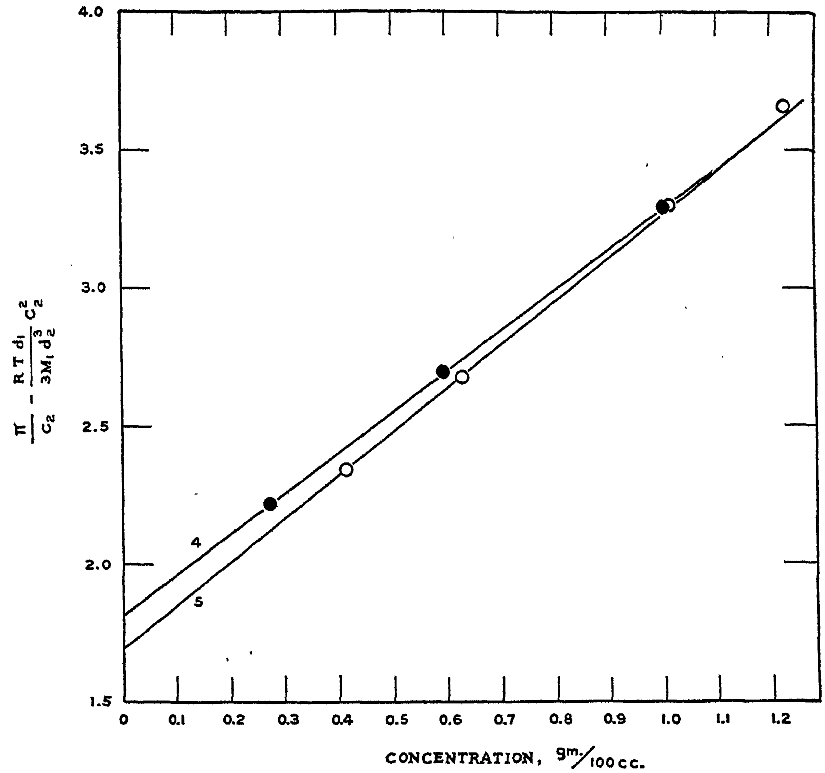

FIG. 6. *Molecular weight of Gelva V 45 with Carter and Record and with caustic treated membranes. 4. Caustic treated membrane. 5. Carter and Record membrane.*

Constancy of Slope

According to Huggins (13), the slopes of the plot π/C_2 versus C_2 or, where significant, $\left(\frac{\pi}{C_2} - \frac{RTd_1}{3M_1d_2^3}C_2^2\right)$ versus C_2, should be independent of molecular weight, as also should be the characteristic constant, μ_1, calculated from it. Flory (8) states that μ_1 should be slightly dependent on molecular weight. Plot 7 and Table IV show that, for three samples of polymethyl methacrylate in chloroform with 2% caustic treated membranes, the slopes vary by only 2.8%. The values of μ_1 are likewise constant within experimental error.

DISCUSSION

With an improved type of osmometer, suitable for use with dilute solutions, difficulties due to leakage of solvent through cellophane gaskets and to formation of bubbles within the osmometer have been largely overcome. While

TABLE IV

CONSTANCY OF SLOPE FOR OSMOTIC PRESSURES OF POLYMETHYL METHACRYLATE IN CHLOROFORM

Caustic treated membrane

——	NDR 474	NDR 471	NDR 359
$\left(\frac{\pi}{C_2} - \frac{RTd_1}{3M_1d_2^3} C_2^2\right)_{C_2 = 0}$	0.635	0.415	0.225
Slope	1.62	1.68	1.67
μ_1	0.427	0.424	0.424
$M_n \times 10^5$	4.05	6.19	11.4

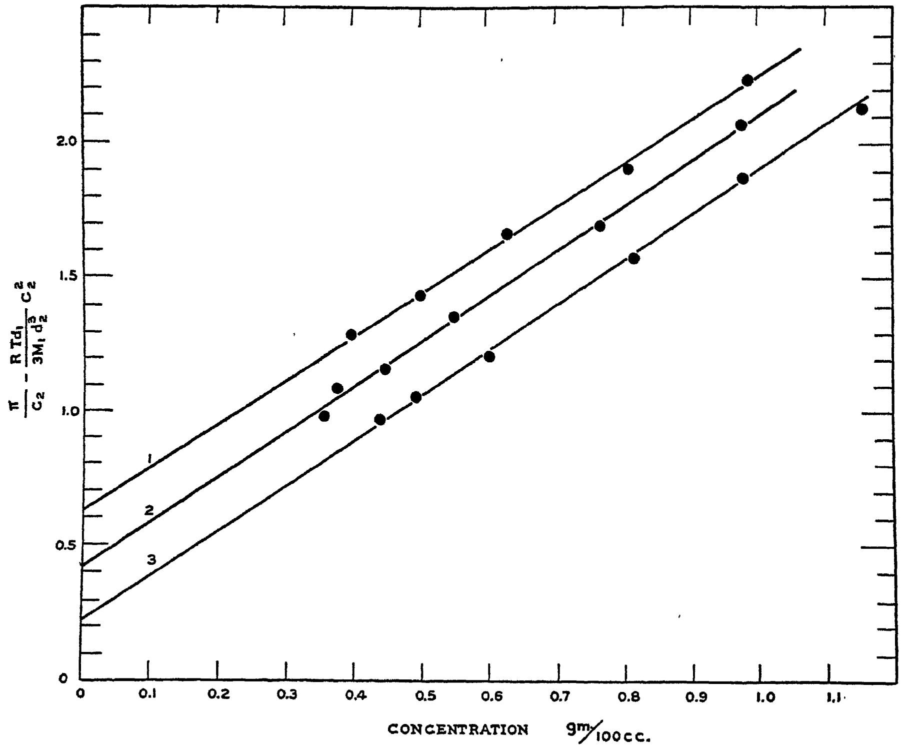

FIG. 7. *Constancy of slope with different molecular weights of polymethyl methacrylate in chloroform. 1. NDR 474. 2. NDR 471. 3. NDR 359.*

it is probable that leakage and bubble formation existed in osmometers used by other workers but were masked by large tubes, it is unlikely, in most cases, that major errors were introduced, since many other workers used corrections to account for finite pressure differences with solvent in both half-cells. Also many workers used membranes of denitrated collodion of very high permeability, which would tend to decrease the error. Nevertheless, trials with both the old types of osmometer and the improved, metal-gasketed type indicate that the metal-gasketed osmometer gives generally better performance and less scattering of points with cellophane membranes.

The major remaining difficulty lies in the tediousness of the determinations. This is mainly due to the time required to eliminate bubbles. The gold plated osmometer in use at present (22) suffers from this difficulty to a much lesser extent. It is conceivable, also, that what bubbles are formed would be eliminated more readily if the cell were equipped with vertical, rather than concentric, grooves. Determinations can generally be made overnight.

With these difficulties in mind, preliminary measurements have been made with a potentially more convenient type of osmometer involving a membrane of copper ferrocyanide (27) deposited in a disk of sintered glass. Promising results have been obtained, although Murray (28) states that such membranes are not suitable for non-aqueous solutions. One membrane has been shown to be semipermeable to a 3% solution of polyvinyl acetate (molecular weight 140,000) in acetone (22). If workable, this type of membrane would have many advantages in simplifying cell design, elimination of membrane flap, etc., and would provide an additional type of membrane for studying the effect of membranes on the observed osmotic values.

The work of Robertson, McIntosh, and Grummitt (32) on membrane preparation has been largely confirmed and extended to show that cellophane membranes, treated with caustic, yield molecular weights differing from those obtained with untreated membranes. It is noteworthy that the curves determined with caustic treated membranes agree with those determined by Robertson, McIntosh, and Grummitt, while those determined with untreated membranes differ decidedly. The reason for the disagreement is not understood.

Using the metal-gasketed osmometer, it has been shown that, for Gelva V 45 in various solvents, the osmotically determined molecular weights are identical within experimental error, although the slopes of the $\frac{\pi}{C}$ versus C curves may vary. The viscosity curves, on the other hand, may give widely differing values for the intrinsic viscosity. It is of interest to note that both the osmotic pressure curves in benzene and acetone and the viscosity curves in benzene and acetone are nearly identical, but vary widely in the case of chloroform. That this behaviour is related to the degree of solvent–solute interaction is shown by the difference between the value of μ_1 for chloroform and for the other two solvents. Huggins' characteristic constant, k', however, determined from viscosity measurements, shows little change from solvent to solvent. It must be concluded, therefore, that this constant is too insensitive to be of much value for the systems studied here.

It is noteworthy that Huggins (14) attributes changes with molecular weight in μ_1 of the order of 0.06 to slight chemical differences in the polymers or to small amounts of impurities. In the present work, the experimental error in μ_1 is estimated from the outside limits of the reproducibility of the osmotic pressure curves as 0.005. It is unlikely, therefore, that Huggins' change of 0.06 can be attributed to experimental error. However, in the present work, for polymethyl methacrylate in chloroform (instead of acetone) no appreciable change of μ_1 with molecular weight has been observed.

Part II

Instability of Solid Polymers

EXPERIMENTAL

In order to eliminate solvation effects on ageing, the changes which take place in solid polyvinyl acetate and polymethyl methacrylate over long periods of time were investigated both in the presence and in the absence of oxygen. For each series a set of three glass bombs of 500 cc. capacity was prepared, each containing 10 to 50 gm. of dry polymer. Samples that were to be aged in vacuum were pumped to a vacuum of 10^{-4} mm., flushed with carbon dioxide, again pumped to 10^{-4} mm. and sealed off. Those to be aged in oxygen were evacuated, flushed with oxygen, re-evacuated, filled with oxygen to a pressure of $\frac{1}{2}$ atm. and sealed off. All bombs were placed in an air-bath at 100 ± 1° C.

Bombs from the various sets were removed periodically, opened, and their contents investigated. In cases where the polymer had fused to the bomb, it was necessary to dissolve out the complete sample, of known weight, in a known quantity of solvent. Aliquots were taken as necessary for investigation. Small quantities of moisture were absorbed during solution and on standing. Consequently the solvent was pumped off the aliquots at room temperature, and the residue taken up with known quantities of dry solvent.

Viscometric and osmotic data were determined as previously described. In addition, in order to investigate any chemical changes during ageing, saponification values were determined on samples of aged polyvinyl acetate by the method of Minsk *et al.* (24).

RESULTS

While polymethyl methacrylate retained its initial whiteness throughout the ageing experiments, the polyvinyl acetate changed in colour from white to pale yellow, the colour deepening with time and being more intense in the polymer aged in oxygen. The Gelva V 15, on account of its low molecular weight, fused to a clear, glassy mass, which underwent the usual colour changes.

Viscosities of aged polymethyl methacrylate were determined both in benzene and in chloroform, while those of polyvinyl acetate were determined in acetone. For each sample, from a plot of $\frac{\ln \eta_r}{C}$ versus C, extrapolated to infinite dilution, the intrinsic viscosity $[\eta]$ and the Huggins, characteristic constant, k', (12), were determined.

Table V summarizes the viscosity data for the polymers studied.

TABLE V

AGEING OF POLYMERS

—			Unaged	In vacuum 2 weeks	In vacuum 3 months	In vacuum 4½ months	In vacuum 6½ months	In oxygen 2 weeks	In oxygen 3 months	In oxygen 4½ months	In oxygen 6½ months
Polymethyl methacrylate											
NDR 359	Benzene	[η] k′	7.96 0.40	7.47 0.41	7.52 0.41	7.55 0.40	7.41 0.40	7.26 0.39	6.86 0.39	6.50 0.37	6.42 0.37
	Chloroform	[η] k′	10.06 0.40	9.76 0.40	9.59 0.40	9.59 0.40	9.48 0.40	9.19 0.39	8.53 0.40	8.65 0.38	8.13 0.40
NDR 471	Benzene	[η] k′	4.28 0.38	4.29 0.38	4.37 0.38	4.28 0.37	4.16 0.38	4.24 0.37	4.09 0.36	3.82 0.35	3.95 0.35
	Chloroform	[η] k′	5.62 0.38	5.59 0.38	5.58 0.37	5.55 0.38	5.39 0.39	5.56 0.38	5.16 0.38	5.04 0.37	4.93 0.39
NDR 474	Benzene	[η] k′	3.58 0.36	3.69 0.39	3.65 0.35	3.54 0.35	3.68 0.36	3.43 0.36	3.47 0.35	3.28 0.35	3.27 0.35
	Chloroform	[η] k′	4.80 0.37	4.84 0.37	4.55 0.37	4.55 0.38	4.72 0.37	4.66 0.37	4.45 0.36	4.17 0.37	4.22 0.38

—		Unaged	In vacuum 24 days	In vacuum 44 days	In vacuum 71 days	In vacuum 76 days	In vacuum 118 days	In oxygen 24 days	In oxygen 51 days	In oxygen 111 days	In oxygen 123 days
Polyvinyl acetate in acetone											
Gelva V 15	[η] k′	0.636 0.35	0.639 0.35	— —	0.644 0.35	— —	— —	— —	0.621 0.34	0.596 0.36	— —
Gelva V 360	[η] k′	2.29 0.37	— —	2.09 0.38	— —	2.06 0.37	2.09 0.37	1.59 0.38	— —	— —	1.50 0.38

For all polymethyl methacrylates in vacuum there is a small decrease in viscosity. For polymethyl methacrylates in oxygen there is an initial rapid decrease in viscosity after which only a slow decrease takes place. The viscosity changes for Gelva V 360 follow the same trend as the polymethyl methacrylates, although the initial decrease in viscosity for polymer aged in oxygen is much sharper. In the case of Gelva V 15, the change in vacuum appears to be within experimental error. In oxygen the viscosity decreases as usual. On account of the fusion of Gelva V 15, access of oxygen to the polymer was probably very limited. As a result, the viscosity change for polymer aged in oxygen is quite small.

Osmotic Pressures

To supplement viscosity data, osmotic pressures were determined on representative samples of polymethyl methacrylate (NDR 359) in chloroform and polyvinyl acetate (Gelva V 360) in acetone. The results are shown in Table VI.

TABLE VI

OSMOTIC PRESSURES OF AGED POLYMERS

—	Unaged	In vacuum 195 days	In oxygen 15 days	In oxygen 90 days	In oxygen 195 days
Polymethyl methacrylate in chloroform					
$\left(\frac{\pi}{C_2} - \frac{RTd_1}{3M_1d_2^3} C_2^2\right)_{C_2=0}$	0.22	0.22	0.33	0.33	0.33
Molecular weight	1.1×10^6	1.1×10^6	7.6×10^5	7.6×10^5	7.6×10^5
μ_1	0.424	0.424	0.424	0.424	0.424
$[\eta]$	10.1	9.48	9.19	8.53	8.13

—	Unaged	In vacuum 118 days	In oxygen 24 days	In oxygen 157 days
Polyvinyl acetate in acetone				
$\left(\frac{\pi}{C_2} - \frac{RTd_1}{3M_1d_2^3} C_2^2\right)_{C_2=0}$	0.74	0.74	1.15	1.22
Molecular weight	3.46×10^5	3.46×10^5	2.20×10^5	2.10×10^5
μ_1	0.440	0.440	0.444	0.443
$[\eta]$	2.29	2.09	1.59	1.42

Although the polymers, when aged in vacuum, changed in viscosity, no corresponding change in osmotic pressure was observed for the two samples tested. In the case of polymers aged in oxygen, the course of the changes in osmotic pressure versus ageing time are very similar to the course for intrinsic viscosity. There is a sharp initial rise in osmotic pressure, after which the osmotic pressure becomes approximately constant. The values of μ_1 show no appreciable change.

Saponification Values

Although any chain scission which took place probably involved a chemical split, no change in saponification value was noted. This is not surprising since the extent of breakage was of the order of one link in 4000.

DISCUSSION

Dispersion in a solvent is not a necessary step for the degradation of polymers. Furthermore, the magnitude of the changes in solid polymers is, in many cases, of the same order as for those aged in solution (21). As expected, further, from the observations of several workers (21, 26) the changes in oxygen were much greater than for polymer aged in vacuum. Morrison, Holmes, and McIntosh (26) have shown that oxygen is used up during the ageing process.

The slowing down of viscosity changes in oxygen after the initial decrease, however, was not due to lack of oxygen, since the addition of further oxygen had little effect. Naunton (29) found that rubber photogels in excess oxygen degrade to a limiting viscosity value. Osmotic pressure determinations by McIntosh and Morrison (21) on samples aged in oxygen showed that the viscosity changes were accompanied by molecular scission. The course of the ageing process can therefore be explained by the presence, at certain points along the chain, of bonds that are weaker than normal and that chain splitting takes place predominantly at these points. This suggestion is in contrast to the assumption of Kuhn (17) that all bonds are of equal strength, in the case of cellulose derivatives, but is supported by Jellineck (15). McDowell and Kenyon (20) suggest that, in the case of polyvinyl acetate, a weak link results from the entry into the polymer chain of oxygen atoms from the peroxide catalyst or acetaldehyde from the vinyl acetate as a chain ending mechanism. This suggestion is in accord with the fact that the rate of degradation of Gelva V 360 becomes very slow when the molecular weight has decreased to roughly half. This indicates only one weak link per molecule as would be the case if the weak link arose out of the chain ending mechanism. The weak links may also represent small amounts of unsaturation in the chains (34), or occasional trisubstituted carbon atoms.

Although, for all polymers aged in vacuum, a small change of intrinsic viscosity occurred, no corresponding change in osmotic molecular weight was noted. In the case of Gelva V 360 aged in oxygen for 157 days, a change of 38% in viscosity corresponds to a change of 82% in osmotic pressure. Yet for the polymer aged in vacuum, the viscosity change of 9% produces no observable change in osmotic pressure. Similarly, for polymethyl methacrylate in oxygen for 15 days, a change in viscosity of 9% corresponds to a change in osmotic pressure of 44%. Yet, in vacuum, a viscosity change of 6% leaves the osmotic pressure unchanged. Furthermore, after the initial decrease in molecular weight of polymethyl methacrylate in oxygen, the osmotic pressure remains constant in spite of a further viscosity drop of 12%. McIntosh and Morrison (21) report that the addition of small amounts of ferric chloride to solutions of polyvinyl acetate in bis(2-chloroethyl) ether causes an immediate increase in intrinsic viscosity with no corresponding change in osmotic pressure.

In this connection, it should be noted that the molecular weight of Gelva V 45 in various solvents has been shown to be constant within 1.5%. This is evidence that the experimental error in the determinations of osmotic pressure is less than 1.5% for this range of molecular weight. For the higher molecular weight Gelva V 360, the experimental error would be 3.7% and for polymethyl methacrylate 12%. However, where no change in osmotic pressure took place (Table VI), the agreement is evidently better than that indicated by the estimated errors. In any case, however, the magnitude of the osmotic pressure changes which would correspond to the viscosity changes is greater than the estimated experimental error. In view, however, of the uncertainty still remaining concerning membrane behaviour, there is some possibility that the effect is not a real one.

Present evidence, nevertheless, suggests that viscosity changes may occur without corresponding changes in molecular weight, possibly as a result of the presence of two independent processes. A similar phenomenon has been reported by Alfrey, Bartovics, and Mark (1) whose samples of polystyrene, prepared at various temperatures, had different viscosities, but similar osmotic molecular weights. The viscosity changes without molecular weight changes could be attributed to alterations in the geometrical configuration of the molecules. Mead and Fuoss (23), for instance, in order to explain viscosity effects, suggest that polymer molecules slowly break up, untangle, and elongate. However, in the present work, the fact that the values of μ_1 for polymers aged in vacuum have not changed is evidence that any changes in shape or degree of solvent–solute interaction which took place were small.

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THE POLAROGRAPHIC DETERMINATION OF TIN IN HIGH PURITY ZINC AND ZINC DIE-CASTING ALLOYS[1]

By R. C. Hawkings,[2] D. Simpson,[3] and H. G. Thode[4]

Abstract

A procedure has been developed for the determination of tin in high-purity zinc and zinc die-casting alloys present in amounts from 0.001 to 0.2%. The samples are dissolved in sulphuric acid, oxidized with hydrogen peroxide, precipitated with cupferron, redissolved and reduced, and finally the tin is determined polarographically. By this method, the tin can be determined with an accuracy of ± 2.0% when present in amounts less than 0.005%. A method is now available for the routine polarographic determination of trace amounts of copper, lead, cadmium, and tin in high-purity zinc and zinc die-casting alloys with a high degree of accuracy and precision.

Introduction

The discovery that trace amounts of lead, cadmium, and tin cause intergranular corrosion in zinc die-casting alloys, which results in a serious weakening of the alloy, makes it important to have available a rapid and accurate method for determining trace amounts of these elements. The spectroscopic method has been applied with a fair degree of success, but the equipment necessary is expensive. Several years ago Hawkings and Thode (2) reported a procedure for the routine polarographic determination of trace amounts of copper, lead, and cadmium. A procedure for the polarographic determination of tin was also developed to complete the group of elements mentioned above. However, publication of the latter procedure has been held up because of security regulations. This paper deals with the determination of trace amounts of tin in the presence of zinc and other metals, and describes a polarographic procedure that has been used successfully for several years.

Smrž (10) made a study of stannous tin and found that in a chloride solution (0.5 to 0.1 N hydrochloric acid) the wave for tin almost coincides with that of lead, and that it was possible to determine tin to 10^{-6} mole per litre, provided the stannous solutions were fresh, free from oxygen, and acidic. He also observed an ageing effect for stannous tin in alkaline solutions, which made the quantitative determination of tin in such a medium difficult. Kalousek (3) studied the redox system of tin and found that stannic chloride is not reducible except in very strong chloride solutions (above 0.1 N) where its reduction appears inhibited. He also observed waves for stannous tin in alkali and citrate solutions. Strubl (11) investigated the anodic oxidation of the stannous tartrate complex. Lingane and Scott (5) were able to obtain

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[2] *Graduate student; now at Northwestern University, Evanston, Ill.*

[3] *Graduate student; now at Purdue University, Lafayette, Indiana.*

[4] *Professor of Chemistry, McMaster University, Hamilton, Ontario.*

waves for stannous tin in 2 *N* perchloric acid and for stannic tin in 2 *N* perchloric acid in the presence of at least 0.5 *N* chloride. Shakhov (9) determined stannous tin in potassium fluocolumbate and metallic columbium (niobium), using an alkaline citrate medium. Winkel and Proske (12) state that in acid and neutral solution, cobalt, lead, and tin (ous) come too close together to give separate waves. In alkaline solutions a good separation is obtained. Cozzi (1) determined tin in white metals by difference from the sum of the lead and tin (ous) waves. The lead alone was determined in alkali medium, and the sum of tin and lead by reduction in acid chloride medium. Seith and Esche (8) also used the method of measurement of difference for tin in zinc. The lead wave alone is obtained by volatilizing the tin as stannic chloride from acid solution.

The work of the above authors indicates that the applications of the polarograph to the determination of tin are nearly always complicated by the fact that the tin (ous) wave is almost coincident with that of lead. The determination of tin by difference is inclined to be inaccurate when the lead concentration exceeds that of the tin by a factor of approximately five. Cozzi (1) partially surmounted this difficulty by making a preliminary separation of most of the lead, but this particular procedure is rather impractical for trace elements in zinc owing to the difficulties of precipitation. The purpose of this investigation was, therefore, to develop an accurate method for the determination of trace amounts of tin (0.001% or less) in high purity zinc die-casting alloys by as direct a method as possible.

Cupferron has been successfully used as a precipitant for the separation of tin from many metals. Attempts to separate tin from lead in zinc alloys met with rapid success and resulted in the present successful method. Lundell and Knowles (7) have surveyed the uses of cupferron as a reagent in quantitative analysis, but make no mention of the determination of tin. The most complete survey of the uses of cupferron in quantitative analysis is presented by Lundell and Hoffman (6), who list in a table the effect of cupferron on the elements of the periodic system when used in 1 : 9 sulphuric or hydrochloric acid. According to this table, cupferron can be used to separate tin and lead in the presence of zinc, magnesium, and aluminium, found in zinc die-casting alloys. However, no mention has been made of the use of cupferron for the separation of micro quantities of tin, of the order of $10^{-2}\%$, particularly in the presence of a large excess of other metal ions such as are found in zinc and zinc die-casting alloys.

Apparatus and Reagents

This work was carried out exclusively with the Heyrovsky Model XI Polarograph (E. H. Sargent and Co.) which has a galvanometer sensitivity of 0.0027μ amp. per mm. The same capillary was used as in the work on copper and lead, and cadmium, and the precautions observed were the same. The electrolysis cell with an external anode was of a design similar to that of Lingane and Laitinen (4) (Fig. 1). The solution of the samples was carried out in 150 ml. beakers which were cooled in a bath of running water prior to precipitation. Filtrations were made with Jena No. 3 sintered glass crucibles, and the precipitate was dissolved in the apparatus shown in Fig. 2. Reductions were carried out in a 50 ml. flask, through which a steady stream of carbon dioxide was passing. After reduction, the flask was cooled to 25° C. and finally after proper dilution a portion of the solution was transferred to the electrolysis cell as shown in the diagram (Fig. 1). A stream of carbon dioxide or nitrogen was maintained through the solution in the electrolysis cell during the transfer, and over the solution when measurements are being made.

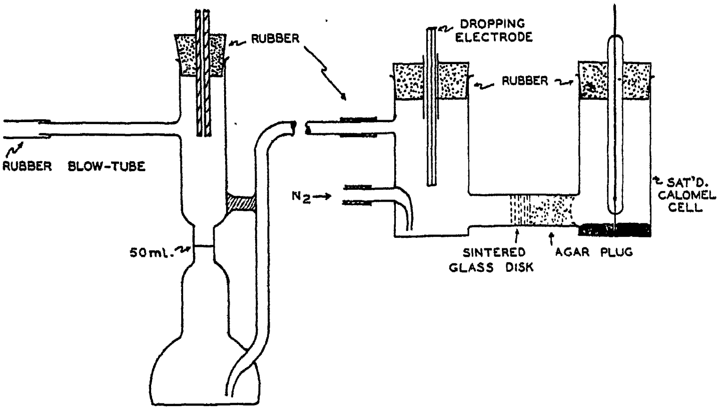

FIG. 1. *Electrolysis cell showing transfer of reduced solution.*

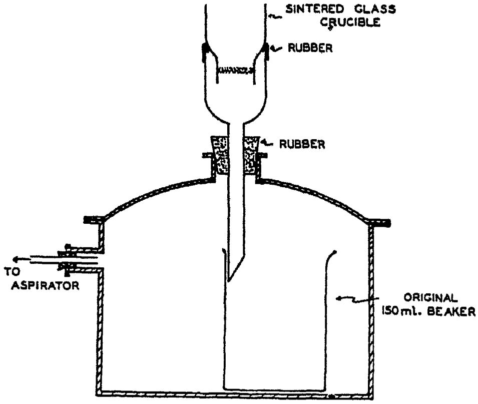

FIG. 2. *Apparatus for solution of precipitate.*

The reagents outlined were tested for tin content by the method of difference. After proper treatment, the residue in each case was added to 10 gm. of analysed zinc, and the whole carried through the procedure for tin. After subtracting the residual current for the tin in the zinc and reagents, the correction for the tin in the reagent tested was obtained. The over-all effect of tin impurities in the reagents used amounted to 0.00011%, which would have to be subtracted from the percentage of tin found in the zinc sample.

Procedure

To 10 gm. of zinc in a 150 ml. Pyrex beaker add 50 ml. of distilled water and 15 ml. of concentrated sulphuric acid (sp. gr., 1.84). When the reaction has subsided, warm on a sand-bath to complete the solution of the zinc. Wash down with distilled water, dilute to 100 ml. and add 5 ml. of 30% hydrogen peroxide. Boil until solution is complete and all hydrogen peroxide is decomposed.* Dilute again to 100 ml., add 5 ml. concentrated hydrochloric acid (sp. gr., 1.19) and cool in running water (15° C. or less).† Add about 3 ml. of a 5% solution of cupferron (stabilized with phenacetin‡) drop by drop with constant stirring. Stir until the precipitate coagulates.§ Stir in approximately 0.1 gm. of Analytical Filter-Aid (Johns–Manville Co.) and filter within half an hour (keep solution cool if allowed to stand with precipitate) using moderate suction on a Jena No. 3 sintered glass filtering crucible. Wash beaker and precipitate with 20 ml. of 0.05% cupferron solution, containing the 1 : 50 sulphuric acid. Dissolve precipitate in the filtering crucible with 10 ml. concentrated nitric acid (used in small portions, e.g., 5 + 5 or 3 + 3 + 4) and wash with water, collecting the filtrate in the original beaker. Add 4 ml. concentrated sulphuric acid and evaporate to fumes. Cool, add 5 ml. nitric acid and evaporate again to fumes. Wash down with 10 ml. of water and warm to dissolve salts. Transfer to a 50 ml. reduction flask, using a rubber policeman to ensure complete transfer. Add 4 ml. concentrated hydrochloric acid and 0.1 gm. pure aluminum foil. Heat gently in a stream of carbon dioxide until clear and then for 15 to 30 min. longer to ensure complete solution of the tin. Cool, add 1.25 ml. of fresh 0.1% gelatin solution and dilute to volume with freshly boiled distilled water. Cool to 25° C., adjust volume, transfer to electrolysis cell, through which a stream of nitrogen is passing, and electrolyse immediately from − 0.3 to − 0.7 v., using a saturated calomel reference electrode. Record polarogram at greatest sensitivity possible.

Results and Discussion

The electrocapillary curve and capillary constant in the medium in which the tin is determined were measured for the purpose of referring results to other capillaries. The temperature of measurement was 25.0° C. and h = 36.5 cm. of mercury.

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* *If solution is not complete add a second portion of hydrogen peroxide. The absence of hydrogen peroxide is indicated by the absence of small bubbles at the surface of the boiling solution. Add extra water if necessary to keep salts in solution.*

† *Cf. section on interference of lead.*

‡ *5% Cupferron (5 gm. B.D.H. cupferron; 0.25 mgm. acetophenetidine (phenacetin)). Dilute to 100 ml.*

§ *Sometimes, in the presence of certain quantities of elements such as lead, arsenic, antimony, or, for unknown reasons, the precipitate will not coagulate. In such an event, filter after 10 min. stirring.*

TABLE I

ELECTROCAPILLARY CURVE

Potential, v.	0 (Cell disconnected)	0 (Cell connected)	−0.3	−0.5	−0.7
Time (25 drops), sec.	78.75, 81.40, 79.60	80.10, 80.30	80.6, 80.5	84.1, 84.3	84.15, 84.25
Drop time, sec.	3.20	3.21	3.22	3.36	3.36

TABLE II

CAPILLARY CONSTANT

Applied potential	Temp., ° C.	No. drops	Time, sec.	Weight, mgm.	$m^{2/3}\,t^{1/6}$
−0.5	24.8	50	168.4	211.7	1.43
−0.5	24.8	50	169.2	213.7	1.43

The capillary was next calibrated for tin by making additions of tin from the diluted stock solution. The calibrations were carried out over a concentration range of 10^{-6} *M* to 3×10^{-3} *M* and the step-heights obtained by difference from the residual current of the tin present in the zinc used as a base. The calibration constants for three successive calibrations are given in Table III.

TABLE III

CALIBRATION CONSTANTS FOR TIN IN ZINC

Added conc. Sn, moles/litre	Per cent added Sn (10 gm. Zn in 50 ml.)	(1) Factor %/μamp.	(2) Factor %/μamp.	(3) Factor %/μamp.	Av. Factor %/μamp.
1×10^{-6}	0.0000_6	0.00375	0.01362	0.02500	0.0141
5×10^{-6}	0.0003_0	0.01428	0.01605	0.01356	0.0146
2.5×10^{-5}	0.0014_8	0.01558	0.01586	0.01756	0.0163
1.25×10^{-4}	0.0074_2	0.01418	0.01645	0.01432	0.0148
6.25×10^{-4}	0.0371	0.01322	0.01347	0.01336	0.0134
3.13×10^{-3}	0.1855	—	0.01264	0.01735	0.0151
				Average factor	0.0147

The factors were obtained in terms of per cent of the metal per microampere of diffusion current for a 10 gm. sample of zinc in 50 ml. of solution for the sake of convenience in calculating the results of analyses.

In order to determine the precision of the method, and to discover the greatest source of error in the procedure, four series of determinations were carried out.

(*a*) Precision of repeated determinations on the same cell, (*b*) Precision of repeated determinations on different aliquots of the same solution,

(*c*) Precision of repeated determinations on different samples of the same alloy,

(*d*) Precision of repeated measurements on same curves for:

  (1) Different individuals,

  (2) The same individual.

TABLE IV

PRECISION OF POLAROGRAPHIC PROCEDURE

Series	Tin		
	Average %	Average deviation, %	Method
(*a*)	0.0020_9	±0.00004	Average deviation from mean of eight runs.
(*b*)	0.0019_0	±0.00003	Average deviation from mean of five runs in duplicate.
(*c*)	0.0021_0	±0.00008	Average deviation from mean of seven samples (duplicate runs).
(*d*) (1)	0.0007_4	±0.00002	Average deviation from mean of two observations on each of six different curves for nine individuals.
(2)	0.0007_3	±0.00002	Average deviation from mean of 10 observations on each of six different curves by the same individual.

It is apparent that the error of reproduction of the curves by the instrument is very small, and that the error is almost entirely that of measurement of curve heights in this case. The error of repeated determinations on different samples is of the same order as the error of measurement of curve heights.

The accuracy of the procedure was determined by the analysis of a series of samples from the National Bureau of Standards, Washington, D.C. The results are shown in Table V.

TABLE V

ACCURACY OF METHOD

EXPERIMENTAL VALUES

(% Sn per 10 gm. of Zn in 50 ml.)

Sample No.	(1)	(2)	Av.	Corrected value	Certificate value
No. 108 spelter	0.0008_3	0.0007_1	0.0007_7	0.0007 ± 0.0001	0.0008
No. 109 spelter	0.0004_2	0.0004_3	0.0004_3	0.0003 ± 0.0001	0.0002
No. 110 spelter	0.0005_4	0.0005_7	0.0005_6	0.0005 ± 0.0001	0.0005
No. 94 Al, Mg, Cu, die-casting alloy	0.0007_2	0.0009_2	0.0008_2	0.0007 ± 0.0001	<0.0005

Table V indicates that within the limit of the precision, the method is accurate to 1 × 10^{-4}% except in the case of the die-casting alloy, where the error is 2 × 10^{-4}%. No explanation is available for the greater error in this case.

Aluminium Reduction

The reduction process used in the procedure for tin was developed in our own laboratory for the purpose on hand, and, as a result, a few essential facts about its manipulation will be given. The process is based upon the fact that metallic aluminium reduces tin to the metallic state quantitatively, and the resulting tin redissolves hydrochloric acid to the stannous state in an inert atmosphere.

Experiments have indicated that from 1 to 10 ml. of concentrated hydrochloric acid is quite satisfactory for amounts of tin up to 0.002%, but 4 to 5 ml. is recommended as ideal, in that the process is neither too slow nor rapid enough to be violent. In the event that the tin content is in excess of 0.007%, an increase in the amount of hydrochloric acid added is advisable. Add 6 ml. hydrochloric acid when tin content is 0.04% and 8 ml. hydrochloric acid when tin content is 0.2%. By this means, the reduction proceeds in a reasonable length of time. Additions of aluminium-foil from 0.025 to 0.05 gm. were tried and were equally successful in the presence of 0.002% tin but 0.5 gm. of aluminium caused a violent action. Aluminium of approximately 0.1 gm. is recommended. Studies of the time of digestion after the solution has lost its turbid appearance indicate that from 15 to 30 min. is the best.

With these refinements, the procedure is satisfactory for tin concentrations up to 0.2%. It should be feasible to use higher concentrations, although this has not been investigated. In such a case, a smaller sample would be preferable.

Interfering Elements

The interference of some 19 elements that may be found in zinc, either as alloying elements, or as impurities, has been considered. They are listed as follows: Sn, Sb, As, Pb, Bi, Cu, Cd, Fe, Ni, Co, Mn, Tl, In, Ag, Hg, Ge, Ga, Al, and Mg.

Of these, tin is to be determined. According to Lundell and Hoffman (6), cupferron in diluted 1 : 9 hydrochloric or sulphuric acid will precipitate Sn, Sb, Bi, Ge, Fe, completely, Cu and Tl incompletely. Furthermore, no precipitation of Sb as Sb^{+++++} will occur. This leaves only Bi, Ga, Fe, Cu, and Tl as possible interfering elements. In a reduced chloride medium Ga and Fe^{++} would not be expected to interfere because their discharge potentials are above that of Sn^{++}. This leaves only Bi, Cu, and Tl as interfering elements from a polarographic point of view, and two of these, Cu and Tl, are known to be incompletely precipitated.

Extensive experiments have shown that there is absolutely no interference from Co, Hg, Mn, Ni, Ag, Fe, Tl, Sb, when these elements are present in amounts of 0.05%. In every case this is more than would normally be expected in high purity zinc or zinc die-casting alloys. The Fe may possibly be an exception to this, but as pointed out above, the Fe^{++} has a discharge potential well above that of Sn^{++}. Cd up to 1% has no detectable effect on the determination of Sn. Bi was tried at the level of 0.05%, and although a black residue appeared in the reduction flask (Bi), the wave for tin was quite normal. Al and Mg were already present in the metal used for the development work in amounts of approximately 4% and 0.1%, respectively. That there is no interference from these elements is borne out by the fact that the calibrations for Sn were made in their presence and the procedure applied with equal success to spelters (cf. B. Stds. No. 108, No. 109, No. 110). In, Ge, and Ga were not tried partially because of the difficulty of procuring the respective salts and partially on the basis of the confirmation of Lundell and Hoffman's work, on elements precipitated by cupferron by the writers. Of the other three, only one, Ga, is expected to precipitate and this has a higher discharge potential than Sn. Arsenic is not expected to precipitate and tests with 0.05% arsenic show no interference from this source.

The two remaining elements, Pb and Cu, were found to give difficulty. The Pb is not precipitated by the cupferron, but is separated with the cupferron precipitate of Sn as lead sulphate which later dissolves in the nitric acid to appear as Pb^{++} in the final solution. Cu is incompletely precipitated and appears in the final solution in the extent to which it is precipitated.

It was found, however, by the addition of 5 ml. concentrated hydrochloric acid to the solution prior to cupferron precipitation, that Pb up to 0.01% can be present without precipitation of lead sulphate. For the determination of Sn in the presence of larger amounts of Pb (up to 1.3% tried) the Pb can be removed by suction filtration on a sintered glass crucible of the oxidized sulphuric acid solution to remove lead sulphate, followed by the addition of 5 ml. hydrochloric acid and the precipitation of the Sn with cupferron. The use of larger amounts of hydrochloric acid is not sufficiently effective to warrant its use.

The interference of Cu presented a more difficult problem. Copper up to 0.04% can be tolerated by the procedure, and even amounts of 0.25% are not impossible, although in this extreme case the limit of detection drops because of the necessity for using a lower galvanometer sensitivity to compensate for the Cu. It was found, however, that by a rapid 30 min. deposition of the Cu from the sulphuric acid solution using 2 amp. at 5 v. and a rotating gauze anode, that 3% of Cu can be removed to such an extent that no interference is found. Experiments indicate Cu from 0.05% to 3% are easily deposited. The deposition is practically quantitative, giving slightly high results for copper, owing to contamination of the deposit. The deposition is not affected by the presence of as much as 0.2% tin which is quantitatively determined in the electrolyte by the usual procedure. Deposition times from 15 to 60 min. were tried and deposition was found to be sufficiently complete in 30 min. for the purpose on hand.

The procedure developed for the polarographic determination of tin in high purity zinc and zinc die-casting alloys is accurate and precise in the presence of 19 elements, which are liable to be present in varying amounts for tin contents ranging from 0.001 to 0.2%. Furthermore, because of the nature of the procedure, it has applications, with suitable modifications, for the microdetermination of tin in numerous other materials without recalibration of the capillary.

It should also be pointed out that although the procedure for tin was developed using a 10 gm. sample of zinc, there is no reason why a larger or smaller sample could not be used. If, for example, a 100 gm. sample is used, it should be possible to detect $1 \times 10^{-5}\%$ of tin following the procedure (with suitable modifications).

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Concerning the Theoretical Aspects of the Reaction of Cyanogen and 1,3-Butadiene

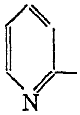
In an earlier communication the reaction of cyanogen with 1,3-butadiene was discussed, and the formation of the product, α-cyanopyridine, was formulated as a Diels–Alder type of reaction in which cyanogen had the role of dienophile (3). This note concerns the thermodynamic considerations of this reaction, and a correlation of these calculations with the experimental results. The thermodynamic approach is of interest and importance in that it enables a schematic picture to be formed of the feasibility of the reactions at various temperatures.

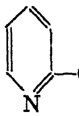
For the present calculations most of the data required were obtainable from those reported in the literature. For butadiene, the heat of formation, 26.748 kcal. (6), the entropy 66.42 cal. deg.$^{-1}$ (12), and the heat capacity equation $C_p^0 = 3.348 + 5.479 \times 10^{-2}\, T - 18.21 \times 10^{-6}\, T^2$ (9) were used. For cyanogen, the heat of formation 71.8_2 kcal. (2) for carbon as graphite, the entropy 57.64 cal. deg.$^{-1}$ (7) and the heat capacity $C_p^0 = 9.982 + 14.48_4 \times \cdot 10^{-3}\, T - 6.207 \times 10^{-6}\, T^2$ (8) were used. For α-cyanopyridine the heat of formation, 62 kcal., was calculated from bond energies and resonance energy, the entropy 77.09 cal. deg.$^{-1}$ and the heat capacity equation $C_p^0 = 14.81_5 + 5.807 \times 10^{-2}\, T - 19.48 \times 10^{-6}\, T^2$ were calculated using the methods of statistical thermodynamics (10, 11) and an assignment of the fundamental vibrational frequencies that was made using the assignment for pyridine reported recently by Kline and Turkevich (5) as a guide. The data for carbon, hydrogen, and nitrogen were taken from Kelley's compilation (4). Using the well known relations between the free energy change, the equilibrium constant, the heat of reaction, and entropy change for a chemical reaction, the values listed in the following table were calculated from these data.

It is a general thermodynamic rule that the free energy change must be favourable for a reaction to be feasible, or that if $\log K_p \geqq 1$, the reaction may be considered as a possible one. In the table above it is seen that, from the values of $\log K_p$, both the synthesis and decomposition of α-cyanopyridine are possible in this temperature range. The low yields of α-cyanopyridine, therefore, which were experimentally observed, are very likely due to the fact that there is a considerable pyrolysis of the product occurring at the temperature of the reaction.

A similar calculation was made for the formation of 1,4-dicyanobutene-2 from cyanogen and butadiene, using the methods and tables of Anderson, Beyer, and Watson (1) to approximate the necessary thermodynamic data. The prediction for this reaction is that it also is a feasible one over the temperature range considered above. However, none of this product was observed in the work reported concerning the reaction of cyanogen and butadiene (3). A possible reason for this is that the 1,4-dicyanobutene-2, lacking the stability against pyrolysis conferred to the α-cyanopyridine by the resonance in the pyridyl nucleus, does not survive the experimental conditions.

VALUES OF LOG K_p IN THE RANGE 300° TO 1200° K FOR THE SYNTHESIS AND DECOMPOSITION OF α-CYANOPYRIDINE

Reaction	(° K) T =	300	400	500	600	700
$CH_2{=}CH{-}CH{=}CH_2 + (CN)_2 =$ (1)  $-CN + H_2$	log K_p =	23.1	16.5	12.6	10.0	8.2
Reaction	T =	800	900	1000	1200	
(1)	log K_p =	6.8	5.7	5.0	3.7	

Reaction	(° K) T =	500	600	700	800	
(2)  $-CN = 6C + 2H_2$ $+ N_2$	log K_p =	35.9	31.6	28.4	26.1	
Reaction	T =	900	1000	1200		
(2)	log K_p =	24.3	22.8	21.0		

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G. J. JANZ

SIR WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,
UNIVERSITY COLLEGE, LONDON.

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THE EVALUATION OF THE INTRINSIC VISCOSITY (AS INTRINSIC FLOW TIME) OF GR-S IN BENZENE[1]

BY L. H. CRAGG,[2] T. M. ROGERS,[3] AND D. A. HENDERSON[4]

Abstract

From careful measurements of the relative flow times of solutions of GR-S in benzene, it has been established that the intrinsic flow time (and hence the intrinsic viscosity) of GR-S in benzene may be most precisely determined by the use of a function $n(t_r^{1/n} - 1)/c$, based on the Baker equation relating η_r, the relative viscosity, and c, the concentration; for the GR-S – benzene system the value of n may be taken as 8. For the greatest precision $[t]$ is determined by linear (horizontal) extrapolation, to zero concentration, of the $8\ (t_r^{1/8} - 1)/c$ vs. c plot; in rapid routine work $[t]$ may be evaluated as $8\ (t_r^{1/8} - 1)/c$ by measurements on only one solution of a concentration such that $t_r = 1.8 \pm 0.4$.

The importance of the intrinsic viscosity $[\eta]$ of a high polymeric substance, as a function empirically and theoretically related to the average chain length of its molecules (34), is now thoroughly established. When the polymeric substance consists of the linear members of a homologous polymeric series (6, 18), intrinsic viscosity is a simple function of the average molecular weight

$$[\eta] = \alpha + KM^{\nu}, \tag{1}$$

where α is negligibly small for *high* polymeric substances (21), and ν is a constant* related to the axial ratio of the molecules (32). Therefore $[\eta]$ is important both in careful studies of the size and shape of high polymer molecules and for following in a routine way the course of various polymeric reactions. For purposes of research, methods of evaluating $[\eta]$ should be accurate; for routine control, they should be rapid and fairly precise. Several methods are widely used at the present time but in both respects they leave a good deal to be desired.

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[2] *Assistant Professor of Chemistry.*

[3] *Senior student.*

[4] *Graduate student, holder of a Bursary under the National Research Council of Canada. Present address: Polymer Corporation, Sarnia, Ont.*

* *If $\nu = 1$, as implicitly assumed by Staudinger, M is the weight average molecular weight; if, as is more usual (25, p. 146), $\nu \neq 1$, M is the 'viscosity average' molecular weight (16), or 'the average for ν equal to a certain value' (22).*

Intrinsic viscosity is a limiting function. Various definitions, such as $\lim\limits_{c \to 0} \eta_{sp}/c$, $\lim\limits_{c \to 0} \frac{\ln \eta_r}{c}$, $\lim\limits_{c \to 0} \frac{d\ \eta_r}{dc}$,* have been shown to be equivalent (11); they all emphasize the fact that ultimately $[\eta]$ must be evaluated by an extrapolation to zero concentration.

Most commonly $[\eta]$ is determined graphically from a plot of either η_{sp}/c or $\frac{\ln \eta_r}{c}$ against c, on the assumption that these curves are linear in the low concentration range; sometimes η_{sp}/c is plotted against η_{sp} (22, 31) or $\frac{\ln \eta_r}{c}$ against η_r (23), and the curve extrapolated; much less frequently η_r is plotted against c, the curve extended to $c = 0$, where $\eta_r = 1$, and the tangent drawn to the curve at that point. The assumption that η_{sp}/c is a linear function of c at very low concentrations, originally made by Staudinger (33, pp. 56 ff.) (and, as we have seen, used as the basis of a standard method of evaluating $[\eta]$), has been justified on theoretical grounds by Huggins (21), and by much experimental work. Relatively accurate extrapolation should therefore be possible. Unfortunately, however, the relation is often linear only at concentrations where precise measurement of η_{sp}/c is impossible;† at higher concentrations deviation from linearity may become marked, especially as $[\eta]$ increases (9). Similar considerations apply to the $\frac{\ln \eta_r}{c}$ vs. c plot, although it has the advantage that $\frac{\ln \eta_r}{c}$ is less dependent on c than is η_{sp}/c. With the advantages of linear extrapolation in mind many investigators have searched for relations between relative viscosity and concentration that would be linear over a wide range. Many equations have been proposed in the last 15 years; they have been compared and evaluated by several authors, perhaps most thoroughly by Hess and Philippoff (19) and by Martin (26). Huggins (21) demonstrated that most of these equations (those proposed by Baker (2), by Fikentscher and Mark (14), by Schulz and Blaschke (31), by Bungenberg de Jong, Kruyt and Lens (5), by Martin (26), by Arrhenius (1), by Hess and Philippoff (19), and by Bredée and de Booys (4)) reduce at very low concentrations to an equation of the form

$$\eta_{sp}/c = [\eta] + K' [\eta]^2 c , \tag{2}$$

the equation which he had arrived at on theoretical grounds. In practice the equations proposed by Martin and by Baker seem to be most widely suitable. Baker's equation (in our notation)

$$\eta_r = (1 + ac)^n , \tag{3}$$

where a and n are constants, has been much used in studies of cellulose and its derivatives, especially in the form given it by Philippoff and Hess (19, 29)

$$\eta_r = \left(1 + [\eta]\ ;\right)^8 . \tag{4}$$

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* *In these expressions* $\eta_r = \eta/\eta_0$ *(the viscosity of solution relative to that of the solvent under the same conditions),* $\eta_{sp} = \eta_r - 1$, *and* c *is the concentration expressed (11) in the units grams solute per 100 ml. solution.* $[\eta]$ *therefore has the dimensions of a specific volume and is expressed in the units dl./gm. (12).*

† *As* c *becomes very small,* η *approaches* η_0 *in value and the difference* $\eta_r - 1$ *becomes very small; under these circumstances, therefore,* η_{sp}/c *is a ratio of two small quantities.*

The equation is however more versatile as originally proposed, for the adjustable constant n makes it possible to adapt the equation to any polymer–solvent system. For our purpose it is more useful in the equivalent form

$$\eta_r = \left(1 + \frac{[\eta]}{n} c\right)^{n\,*} \tag{5}$$

The Martin equation

$$\log \eta_{sp}/c = \log [\eta] + K [\eta] c\ , \tag{6}$$

is closely related to that originally proposed by Bungenberg de Jong, Kruyt and Lens and used by Staudinger (35) in the form

$$\begin{aligned} \log \eta_{sp}/c &= \log [\eta] + K_{st}\, c \\ &= \log [\eta] + (K_{mst} + b)\, c \end{aligned} \tag{7}$$

but it has the advantage that it eliminates the second constant b. As a result of a graphical comparison of the various equations Martin (26) has concluded that his is the one most generally suitable, and the plot to be preferred for the determination of $[\eta]$ is that of $\log \eta_{sp}/c$ vs. c. Howlett, Minshall, and Urquhart (20), on the other hand, concluded from a very thorough study with data on cellulose in cuprammonium that the Baker equation was the best of those available. They used it in the form

$$\eta_r^{1/n} = 1 + \frac{[\eta]}{n} c \tag{8}$$

and showed that when $n = 8$ the data gave a straight line over a wide concentration range.

In our experience with the synthetic rubber GR-S (in benzene) the most commonly used methods of determining $[\eta]$ by graphical extrapolation were disappointing. The work of Howlett *et al.* and of Martin encouraged us to undertake a comparison of various methods as applied to the GR-S – benzene system.

Experimental

Materials

The rubber used was a sample of normal commercial GR-S obtained from Polymer Corporation, Sarnia, on October 27, 1945. It was gel-free when received and, stored in air in the dark, remained so during the period of experimentation. In the experiments reported here the GR-S was not extracted with the ethanol–toluene azeotrope to remove non-rubber constituents as we were more interested in the behaviour of GR-S as ordinarily used, but preliminary tests satisfied us that these constituents did not affect the viscosity of the rubber other than by acting as a simple diluent.

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* *When c is very small, Equation (3) reduces to $\eta_r = 1 + nac$.*

Hence $$\left(\frac{d\ \eta_r}{dc}\right)_{c\to 0} = na = [\eta],\ \text{and}\ a = \frac{[\eta]}{n}\ .$$

It is interesting to note that Baker used the constant 'na' to characterize polymer–solvent systems 25 years before the name 'intrinsic viscosity' was introduced and almost 20 years before Staudinger and others demonstrated the importance of the limiting reduced viscosity.

It should be noted that Baker expressed concentration in the units grams per 100 cc. solution, Philippoff in grams per 100 gm. solution (see reference 29, pp. 168-169). Except when the density of the solvent is unity, then, Philippoff's $[\eta]$ is not strictly speaking the intrinsic viscosity as we define it (11, 24).

The solvent used was technical benzene (obtained from the Steel Company of Canada, Hamilton) freed from thiophene by extraction with concentrated sulphuric acid and purified by fractional distillation. The material used boiled in the range 80° to 80.5° C. and gave a negative test with isatin.

Apparatus

Viscosities were determined from measurements of flow time in an Ostwald – Cannon–Fenske capillary viscometer, A.S.T.M. No. 50. This type of viscometer was chosen for use because it is rugged, relatively inexpensive, readily available, and in wide use for routine viscometry. The particular instrument used had the following characteristics:

L, length of capillary, measured	7.3	cm.	
R, radius of capillary,*	0.022_2	cm.	
H, mean hydrostatic pressure head (loading volume, 10 ml.)	8.95	cm.	(head at $t/2$ sec.)
t, time of efflux at 25° C.			
for benzene	171.0	sec.	
for water	220.5	sec.	
V, volume of efflux (vol. between marks)	3.25	$cm.^3$	

Whence:

LT/V (for benzene) $= 3.84 \times 10^2$

HR/L $= 0.027$

τ, mean shearing stress at the wall ($HdgR/2L$), $= 11.7$ dynes per $cm.^2$

The viscometer was therefore of such dimensions that the kinetic energy correction is small enough to be neglected in routine work (the error in intrinsic viscosity caused by neglecting it was found to be of the order of 2%), and the mean rate of shear falls within the range accepted arbitrarily as standard for determining the intrinsic viscosity of GR-S in benzene (15). The charging volume of liquid, 10.0 ml., was measured in a pipette, the same pipette being used for every loading. For measurements of relative flow time t_r (the ratio of flow time of solution to that of solvent at the same temperature) the actual volume loaded need not be known exactly so long as it is kept constant. (With a constant charging volume of 5 ml., the relative flow time is the same, within experimental error, as with one of 10 ml.) The effect on the volume of differences in rate of draining from the pipette was proved to be insignificant over the range of concentrations employed.

Temperatures were controlled by means of a constant temperature bath, which consisted of water in a 12 by 12 in. cylindrical Pyrex jar heavily lagged with asbestos (through which windows were cut for observation). The bath was provided with an efficient stirrer, a cooling coil, and a heater controlled by a thermoregulator of the de Khotinsky type protected by an electronic relay; by these means the temperature was kept uniform throughout the bath liquid and constant to ± 0.01° C. The viscometer was supported on the edge of the jar in correct vertical alignment by means of a specially designed clamp. Measurements of temperature were made with a calibrated thermometer; and the flow times were measured with a calibrated stopwatch read to 0.1 sec.

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* *Calculated from the Poiseuille formula,* $\eta = \pi R^4 H g d t/8 L V$, *using the following values:* $d_{25} = 0.873$ *gm./ml.,* $\eta_{25} = 0.00603$ *poise,* $g = 981$ *cm./sec.*$^{-2}$

Procedure

Solutions were prepared by dissolving weighed samples of GR-S in benzene and then making the solution up to volume; concentrations are therefore expressed as gm. per 100 ml. solution. A portion of GR-S was cut into cubes (approximately 1 mm.^3), the desired amount weighed to 0.1 mgm., introduced into a dry 100 ml. volumetric flask, covered with 90 ml. solvent, and allowed to stand undisturbed in the dark for 24 hr., whereupon solution was complete. (Since the polymer was gel-free the solution was not filtered except when extraneous material was obviously present.) The solution was brought to 25.00 ± 0.01° C. by suspending the flask in the bath for at least 10 min., and then, after gentle but thorough mixing, benzene at the same temperature was added to a total volume of 100.0 ml.

Measurements of flow time were made in duplicate or triplicate with each loading and repeated on successive loadings until agreement within ± 0.1 sec. was obtained. At regular intervals the flow time of pure solvent was redetermined to make sure that no particle had lodged in the capillary. After each run the viscometer and pipette were cleaned with benzene, by filling and emptying twice and then flushing thoroughly, and dried with air filtered through absorbent cotton and a fine sintered-glass disk.

Experimental Data

Measurements of flow time were made with solutions covering the concentration range 0.05 to 1.0% (grams per 100 ml. solution); and these are recorded as relative flow times. If the kinetic energy correction were really negligible then the relative flow time t_r would be equal to the relative kinematic viscosity, ν_r; if the density of the solutions were the same as that of the solvent, then $t_r = \nu_r = \eta_r$, the relative viscosity. In many investigations density differences and kinetic energy corrections are assumed negligible (or ignored!) and measurements of relative flow time are recorded as relative viscosities. The term 'relative flow time' (11) is much less ambiguous and, for our purposes, just as useful. Since in our work the kinetic energy correction is small and the rate of change in density with concentration very small, t_r is for practical purposes a measure of η_r and $[t]$ a measure of $[\eta]$.

In work of this kind it is common practice to prepare the various solutions by successive dilution of the most concentrated solution. This is particularly true of the most dilute solutions, for if they were prepared directly slight errors in sampling or weighing would disproportionately affect the results. In order to test the various equations relating viscosity and concentration, and at the same time indicate the precision and reproducibility of the data, 25 solutions were prepared by successive dilution of five original solutions (*A*, *B*, *C*, *D*, and *E*) made up, as described above, using samples of GR-S from widely separated portions of a 7 lb. bale. In Table I, *A*-1, *A*-2, *A*-3, *A*-4, are the solutions prepared from Solution *A*, *B*-1, *B*-2, *B*-3, *B*-4 from *B*, etc. (*D*-3 and *D*-4 unfortunately never reached the viscometer!) To replace *D*-4, a solution *F*-4 was made up by successive dilution of one whose concentration was 0.4192 gm. per 100 ml. solution. The measurements on a given series were made at one time to minimize any possible effects due to ageing, incipient gel-formation, etc.

In Table I are given the measured values of t, the flow time, and the calculated values of $t_r^{1/n}$ for $n = 1, 3, 5, 6, 7, 8, 9, 10$, and 12. These are the data necessary for testing the Baker equation.

TABLE I

RELATIVE FLOW TIME FUNCTIONS

Viscometer *A*-25. Temp., 25.00 ± 0.01° C. Solvent: technical benzene (freed from thiophene) redistilled.

$t_0 = 171.0$ sec.

Soln. No.	Concentration, gm. GR-S/100 ml. soln.	t	Log t_r	t_r^1	$t_r^{1/3}$	$t_r^{1/5}$	$t_r^{1/6}$	$t_r^{1/7}$	$t_r^{1/8}$	$t_r^{1/9}$	$t_r^{1/10}$	$t_r^{1/12}$
A	1.0049	970.6	0.75405	5.6761	1.7838	1.4152	1.3356	1.2815	1.2424	1.2127	1.1896	1.1557
B	0.9004	841.5	0.69205	4.9210	1.7009	1.3753	1.3042	1.2556	1.2204	1.1937	1.1728	1.1420
C	0.8000	728.2	0.62924	4.2583	1.6209	1.3361	1.2731	1.2300	1.1986	1.1747	1.1559	1.1281
D	0.7072	633.2	0.56854	3.7031	1.5471	1.2993	1.2438	1.2056	1.1779	1.1566	1.1399	1.1153
E	0.6010	536.7	0.49673	3.1386	1.4640	1.2570	1.2100	1.1775	1.1537	1.1355	1.1212	1.1000
A-1	0.5025	455.7	0.42569	2.6650	1.3864	1.2166	1.1775	1.1503	1.1304	1.1151	1.1030	1.0851
B-1	0.4502	415.2	0.38526	2.4280	1.3441	1.1942	1.1594	1.1351	1.1173	1.1036	1.0928	1.0767
C-1	0.4000	378.2	0.34472	2.2115	1.3029	1.1720	1.1414	1.1200	1.1043	1.0922	1.0826	1.0684
D-1	0.3536	346.2	0.30634	2.0246	1.2650	1.1515	1.1248	1.1060	1.0922	1.0815	1.0731	1.0605
E-1	0.3005	314.7	0.26490	1.8403	1.2254	1.1297	1.1070	1.0910	1.0792	1.0701	1.0629	1.0521
A-2	0.2512	285.2	0.22216	1.6678	1.1861	1.1077	1.0890	1.0758	1.0660	1.0585	1.0525	1.0435
B-2	0.2251	270.5	0.19917	1.5819	1.1651	1.0960	1.0794	1.0679	1.0590	1.0523	1.0469	1.0389
C-2	0.2000	257.9	0.17845	1.5082	1.1467	1.0856	1.0709	1.0604	1.0527	1.0467	1.0419	1.0348
D-2	0.1768	245.6	0.15723	1.4363	1.1283	1.0751	1.0622	1.0531	1.0463	1.0410	1.0369	1.0306
E-2	0.1503	232.6	0.13361	1.3603	1.1080	1.0635	1.0526	1.0449	1.0392	1.0348	1.0312	1.0260
A-3	0.1256	220.8	0.11100	1.2913	1.0889	1.0524	1.0435	1.0372	1.0325	1.0288	1.0259	1.0215
B-3	0.1126	215.2	0.09984	1.2585	1.0796	1.0470	1.0390	1.0334	1.0292	1.0259	1.0232	1.0193
C-3	0.1000	209.9	0.08901	1.2275	1.0707	1.0418	1.0347	1.0297	1.0260	1.0230	1.0207	1.0172
D-3	0.0884	205.0	0.07875	1.1986	1.0623	1.0369	1.0306	1.0262	1.0229	1.0203	1.0183	1.0152
E-3	0.0751	199.9	0.06781	1.1690	1.0533	1.0317	1.0263	1.0225	1.0197	1.0175	1.0157	1.0131
A-4	0.0628	194.8	0.05659	1.1394	1.0445	1.0264	1.0220	1.0188	1.0164	1.0146	1.0131	1.0109
B-4	0.0563	192.3	0.05098	1.1248	1.0400	1.0238	1.0198	1.0170	1.0148	1.0131	1.0118	1.0099
C-4	0.0500	189.8	0.04530	1.1102	1.0355	1.0211	1.0176	1.0150	1.0131	1.0116	1.0105	1.0087
F-4	0.0262 •	180.4	0.02324	1.0550	1.0180	1.0108	1.0090	1.0077	1.0067	1.0060	1.0054	1.0045

Discussion of Results

(1) *The Most Suitable Form of the Baker Equation*

If the equation

$$t_r = \left(1 + \frac{[t]}{n} c\right)^n \qquad (9) \text{ cf. } (5)$$

fits the data, then

$$t_r^{1/n} = 1 + \frac{[t]}{n} c ,$$

and a plot of $t_r^{1/n}$ vs. c should give a straight line. When the data of Table I were so plotted it was found that a straight line over the widest range of concentration was obtained with $n = 7$ or 8 or 9, and that (as might be expected) there was little to choose between these values (see Fig. 1). It is, however, difficult to compare the plot on one graph as the lines all converge at the origin ($t_r^{1/n} = 1$, $c = 0$).

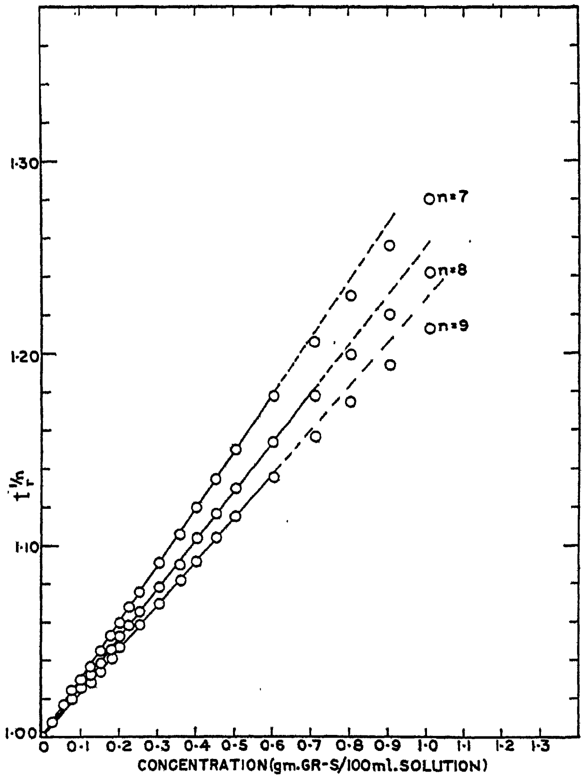

FIG. 1. $t_r^{1/n}$ *vs.* c, *for* $n = 7, 8,$ *and* 9.

If however, the relation between $t_r^{1/n}$ and c is linear over a range of concentrations, then the slope $\frac{d\,(t_r^{1/n})}{dc}$ is constant and is equal to $(t_r^{1/n} - 1)/c$ for any value of c within that range. In other words a plot of $\frac{t_r^{1/n} - 1}{c}$ vs. c is a horizontal straight line so long as the $t_r^{1/n}$ vs. c curve is linear. In Fig. 2, $\frac{t_r^{1/n} - 1}{c}$ is plotted against c for the various values of n. From this figure it is apparent that the best values of n are 7 to 9.

Since the slope of the straight line is $\frac{[t]}{n}$, the intrinsic flow time

$$[t] = \left(\frac{t_r^{1/n} - 1}{c}\right) n\,. \tag{10}$$

A plot of $n\left(\frac{t_r^{1/n}-1}{c}\right)$ vs. c will therefore not only be a horizontal straight line but can be extrapolated in the simplest possible way to $c = 0$ to obtain the value of $[t]$. In Fig. 3 the curves are plotted, for $n = 7$, 8, and 9, from the data of Table II. Again it is evident that there is little to choose between the three, and even less between 7 and 8. Other things being equal, or very nearly so, the value $n = 8$ was chosen because this is the value found most suitable by Howlett for cellulose, and cellulose acetate, solutions and by Philippoff for a variety of high polymer solutions. The precision of our measurements scarcely justifies a selection on any other grounds; measurements of a higher order of precision (30) might make it possible to choose a value of n with greater confidence.

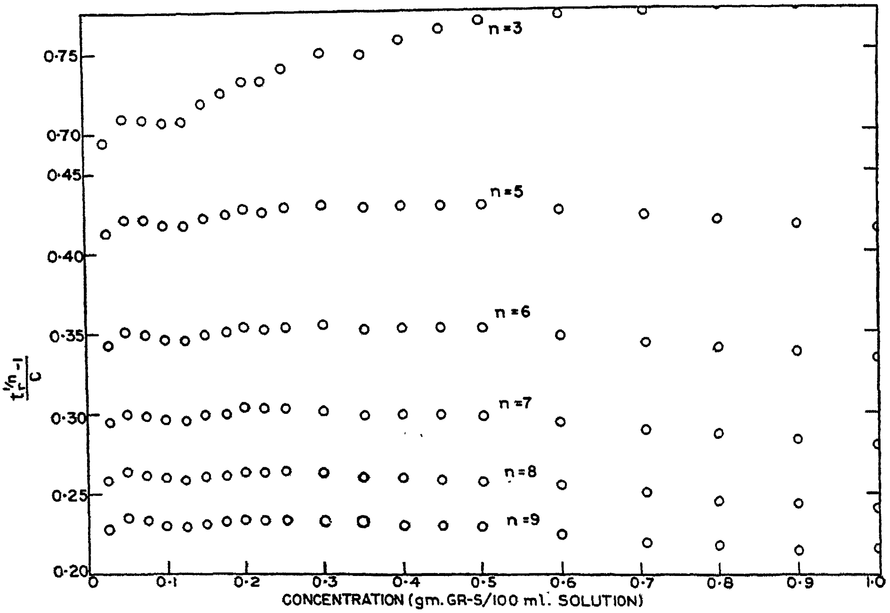

FIG. 2. $\frac{t_r^{1/n}-1}{c}$ *vs.* c, *for* $n = 3, 5, 6, 7, 8,$ *and* 9.

(2) *Comparison of Plots*

A plot of $n\left(\frac{t_r^{1/n}-1}{c}\right)$ vs. c gives a value of $[t] = 2.09 \pm 0.02$ whether $n = 7$, 8, or 9 (Fig. 3). The other functions that are in common use, or that have been strongly recommended, for evaluating $[t]$ have been plotted in Figs. 4, 5, and 6, from the data of Table III.

It is evident (Fig. 4) that the inherent flow time $\frac{\ln t_r}{c}$ (11), does not give a horizontal straight line. A line can be drawn through the points that will give $[t] = 2.09$, and it is a good choice; but without this guidance a choice of the most suitable line, and particularly of the most suitable slope of the

TABLE II

CALCULATED VALUES OF $n\left(\frac{t_r^{1/n}-1}{c}\right)$

Soln. No.	Concentration, gm. GR-S/100 ml. soln.	$n = 1$	$n = 3$	$n = 5$	$n = 6$	$n = 7$	$n = 8$	$n = 9$	$n = 10$	$n = 12$
A	1.0049	4.65	2.34	2.07	2.00	1.96	1.93	1.91	1.89	1.86
B	0.9004	4.35	2.34	2.08	2.03	1.99	1.96	1.94	1.92	1.89
C	0.8000	4.07	2.33	2.10	2.05	2.01	1.99	1.97	1.95	1.92
D	0.7072	3.82	2.32	2.11	2.07	2.04	2.01	1.99	1.98	1.96
E	0.6010	3.56	2.32	2.14	2.10	2.07	2.05	2.03	2.02	1.99
A-1	0.5025	3.24	2.31	2.15	2.12	2.09	2.07	2.06	2.05	2.03
B-1	0.4502	3.17	2.29	2.15	2.12	2.10	2.08	2.07	2.06	2.04
C-1	0.4000	3.03	2.27	2.15	2.12	2.10	2.09	2.08	2.07	2.05
D-1	0.3536	2.90	2.25	2.14	2.12	2.10	2.09	2.07	2.07	2.05
E-1	0.3005	2.80	2.25	2.16	2.14	2.12	2.11	2.10	2.09	2.08
A-2	0.2512	2.66	2.22	2.14	2.13	2.11	2.10	2.10	2.09	2.07
B-2	0.2251	2.58	2.20	2.13	2.12	2.11	2.10	2.09	2.08	2.07
C-2	0.2000	2.54	2.20	2.14	2.13	2.11	2.11	2.10	2.09	2.08
D-2	0.1768	2.47	2.17	2.12	2.11	2.10	2.10	2.09	2.09	2.07
E-2	0.1503	2.39	2.16	2.11	2.10	2.09	2.09	2.08	2.07	2.07
A-3	0.1256	2.32	2.12	2.09	2.08	2.07	2.07	2.06	2.06	2.05
B-3	0.1126	2.29	2.12	2.09	2.08	2.08	2.08	2.07	2.06	2.05
C-3	0.1000	2.27	2.12	2.09	2.08	2.08	2.08	2.07	2.07	2.06
D-3	0.0884	2.25	2.11	2.09	2.08	2.08	2.07	2.07	2.07	2.06
E-3	0.0751	2.25	2.13	2.11	2.10	2.11	2.10	2.10	2.09	2.08
A-4	0.0628	2.22	2.13	2.10	2.10	2.10	2.09	2.09	2.08	2.07
B-4	0.0563	2.22	2.13	2.11	2.11	2.10	2.10	2.09	2.10	2.08
C-4	0.0500	2.20	2.13	2.11	2.11	2.10	2.10	2.09	2.10	2.08
F-4	0.0262	2.10	2.06	2.06	2.05	2.06	2.05	2.06	2.07	2.06

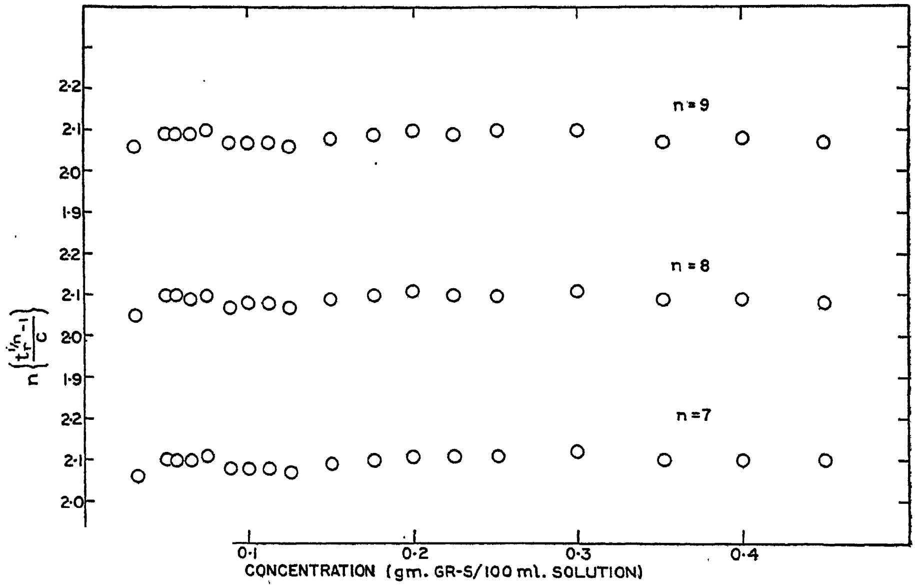

FIG. 3. $n\left(\frac{t_r^{1/n}-1}{c}\right)$ *vs. c, for n = 7, 8, and 9.*

TABLE III

VALUES OF VARIOUS FLOW TIME FUNCTIONS

Solution No.	Concentration, gm. GR-S/100 ml. soln.	$8\left(\frac{t_r^{1/8}-1}{c}\right)$	$\frac{t_{sp}}{c}$	t_{sp}	$\frac{\ln t_r}{c}$	$\log \frac{t_{sp}}{c}$
A	1.0049	1.93	4.65	4.68	1.73	0.6678
B	0.9004	1.96	4.36	3.92	1.77	0.6390
C	0.8000	1.99	4.07	3.26	1.81	0.6099
D	0.7072	2.01	3.82	2.70	1.85	0.5823
E	0.6010	2.05	3.56	2.14	1.90	0.5512
A-1	0.5025	2.07	3.24	1.67	1.95	0.5203
B-1	0.4502	2.08	3.17	1.43	1.97	0.5014
C-1	0.4000	2.09	3.03	1.21	1.99	0.4813
D-1	0.3536	2.09	2.90	1.03	2.00	0.4620
E-1	0.3005	2.11	2.80	0.84	2.03	0.4465
A-2	0.2512	2.10	2.66	0.67	2.04	0.4246
B-2	0.2251	2.10	2.58	0.58	2.03	0.4123
C-2	0.2000	2.11	2.54	0.51	2.05	0.4048
D-2	0.1768	2.10	2.47	0.44	2.05	0.3925
E-2	0.1503	2.09	2.39	0.36	2.05	0.3797
A-3	0.1256	2.07	2.32	0.29	2.04	0.3652
B-3	0.1126	2.08	2.29	0.26	2.04	0.3606
C-3	0.1000	2.08	2.27	0.23	2.05	0.3566
D-3	0.0884	2.07	2.25	0.20	2.05	0.3515
E-3	0.0751	2.10	2.25	0.17	2.08	0.3515
A-4	0.0628	2.09	2.22	0.14	2.08	0.3463
B-4	0.0563	2.10	2.22	0.13	2.09	0.3457
C-4	0.0500	2.10	2.20	0.11	2.09	0.3432
F-4	0.0262	2.05	2.10	0.06	2.04	0.3221

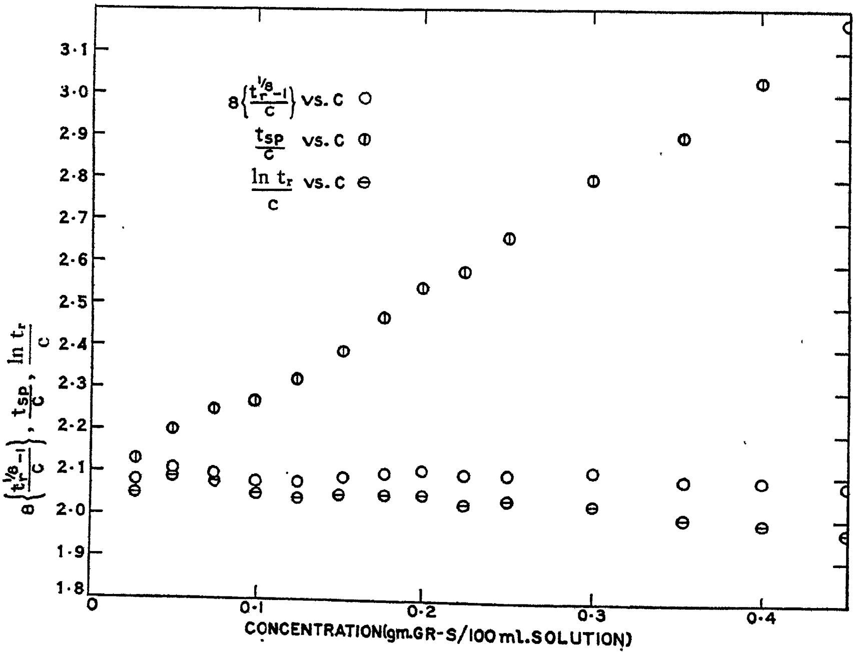

FIG. 4. *Comparison of* $8\left(\frac{t_r^{1/8}-1}{c}\right)$ *vs. c with the two most widely used plots.*

line, is difficult. The advantage of $8\left(\frac{t_r^{1/8}-1}{c}\right)$ vs. c is that the slope is known; the line chosen must be horizontal. (This point has been well made by Howlett *et al.*)

The reduced flow time, $\frac{t_{sp}}{c}$, has the added disadvantage that it gives a *curved* line. An extrapolation is not only difficult but gives most weight to the points that can least bear it, namely, those in the low concentration range (*vide supra*). It is, however, easy to draw a curve that will extrapolate to 2.09. Log $\frac{t_{sp}}{c}$ gives a straight line (Fig. 5)—and one that is relatively easily selected—over the same range as $8\left(\frac{t_r^{1/8}-1}{c}\right)$, and the value of $[t]$ obtained by extrapolation is again 2.09. This plot, although superior to those involving $\frac{\ln t_r}{c}$ and $\frac{t_{sp}}{c}$, appears to have no advantage over $8\left(\frac{t_r^{1/8}-1}{c}\right)$ vs. c, and has the disadvantage that determinations of t_r for at least three solutions of different concentrations would be required to fix the position of the line. (The slope is *not* independent of molecular weight. See Equations (6) and (7).)

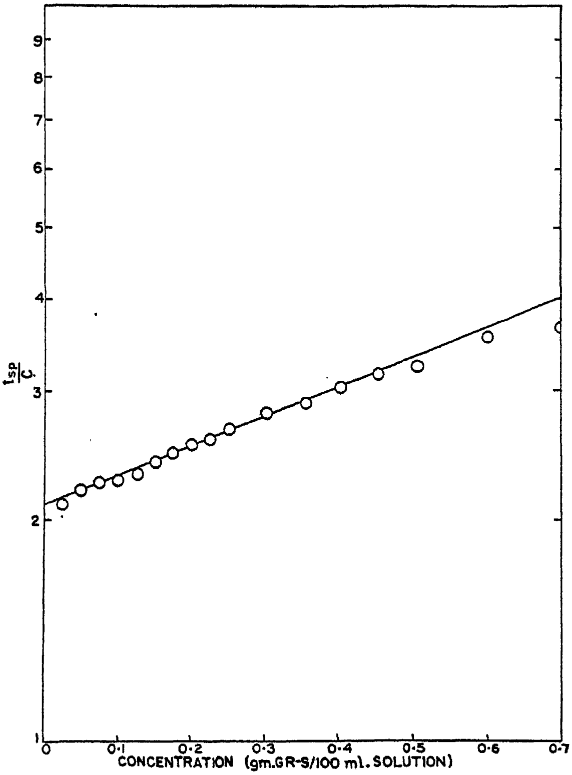

FIG. 5. *log* t_{sp}/c *vs.* c.

Advantages have been claimed for the t_{sp}/c vs. t_{sp} plot, among them that it yields a straight line over a wide range and that it has a sound theoretical background (10). From Fig. 6 it is obvious that, for this system at least, it is inferior to either log t_{sp}/c, c or $8\left(\frac{t_r^{1/8}-1}{c}\right)$, c. And not too much should be made of the theoretical support, for in arriving at the equation

$$\eta_{sp}/c = [\eta]\,(1 + K'\,\eta_{sp}), \tag{11}$$

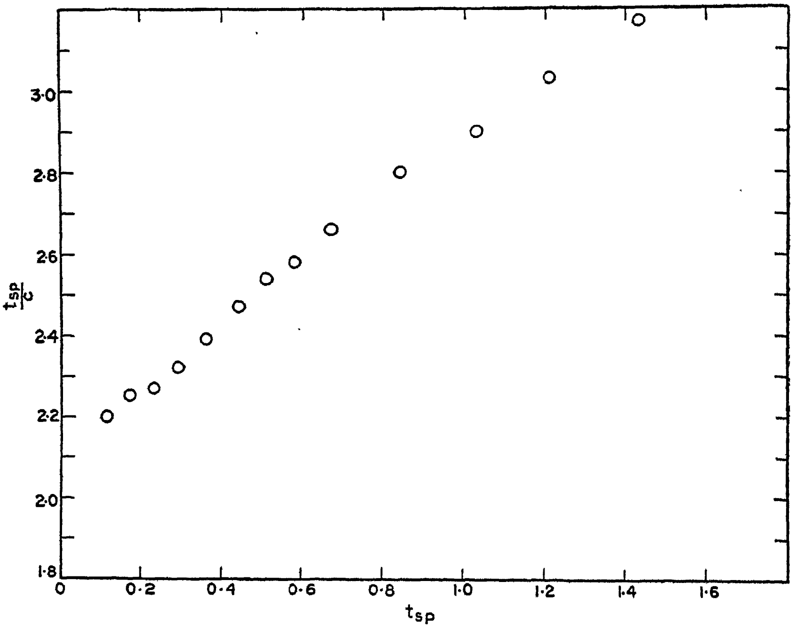

FIG. 6. t_{sp}/c vs. t_{sp}.

Huggins (21) introduced an empirical constant K' to take account of "the sizes, shapes and cohesional properties of both solvent molecules and solute submolecules". The value of K' is obtained experimentally or by calculation from the empirical constants of other equations.

We conclude, then, that, for this system at least, the most satisfactory methods of determining $[t]$—and therefore $[\eta]$—involve extrapolation of curves obtained by plotting $\frac{\ln t_r}{c}$, or log $\frac{t_{sp}}{c}$, or $n\left(\frac{t_r^{1/n}-1}{c}\right)$, against c; and of these the last is the most precise. Indeed the evidence given here leads to the conclusion that it is two or three times as precise as the other two, and many other experiments in this laboratory tend to confirm it. Table IV and Fig. 7 give the results of one such experiment on another sample of plant-run GR-S. Here the intrinsic flow time is 2.20, and again the method gives a value of $[t]$ with a precision of ± 1% or better. The horizontal line might be drawn through any *one* of the points to yield a value of $[t]$ in this range; lines drawn through the minimum two points on the $\frac{\ln t_r}{c}$, c plot give values

TABLE IV

TYPICAL VALUES OF THREE FLOW TIME FUNCTIONS FOR PLANT GR-S
(Sample received from Sarnia, July 17, 1945)

Solution No.	Concentration, gm. GR-S/100 ml. soln.	t_r	$8\left(\frac{t_r^{1/8}-1}{c}\right)$	$\frac{t_{sp}}{c}$	$\frac{\ln t_r}{c}$
1	0.3132	1.952	2.22	3.04	2.14
2	0.2513	1.704	2.19	2.80	2.12
3	0.2035	1.552	2.22	2.71	2.16
4	0.1524	1.386	2.19	2.54	2.14
5	0.1030	1.252	2.21	2.44	2.18
6	0.0805	1.189	2.18	2.35	2.15
7	0.0431	1.101	2.22	2.34	2.22
8	0.0201	1.046	2.22	2.28	2.22

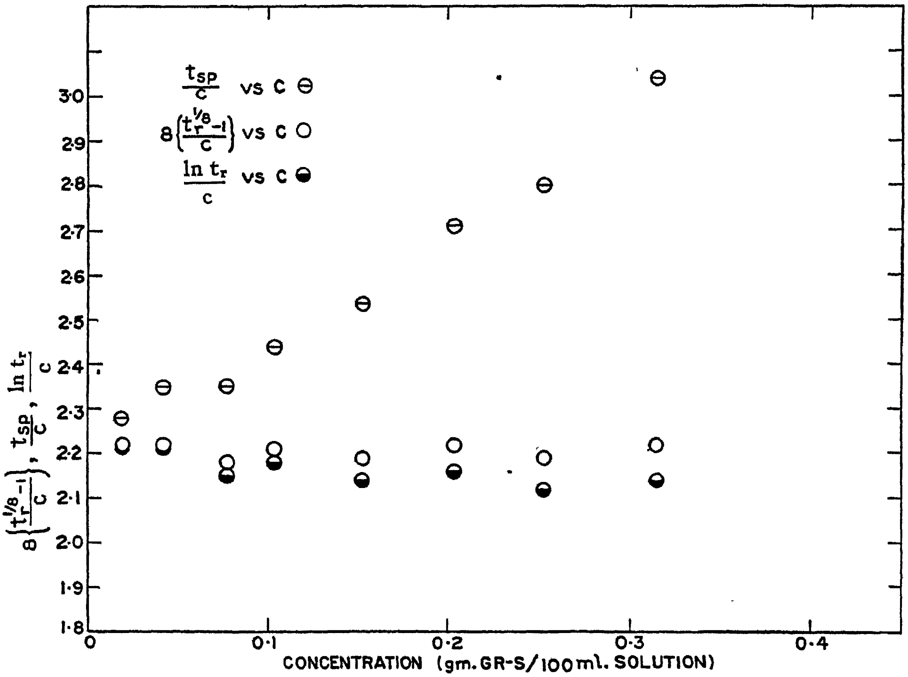

FIG. 7. *Viscosity-concentration relations; second sample of GR-S.*

ranging between 2.0 and 2.35, and, through three well-scattered points, values of 2.15 and 2.23!

It seems reasonable to conclude therefore that the intrinsic flow time of unfractionated GR-S in benzene may be determined most precisely by horizontal linear extrapolation of a curve relating $8\left(\frac{t_r^{1/8}-1}{c}\right)$ and c, or, what amounts to the same thing, averaging several values of $8\left(\frac{t_r^{1/8}-1}{c}\right)$ within the range $c = 0.10$ to 0.45 (or, better, $t_r = 1.2$ to 2.4).

(3) *General Validity of the Method for GR-S – Benzene Systems*

The method here recommended has been equally satisfactory with many samples of normal GR-S of different intrinsic viscosity, made in the plant at Sarnia at different times. To be of maximum value it should, however, be applicable to rubbers of the GR-S type polymerized under widely varying conditions: with different charge ratios of monomers, with various modifiers, to different conversions, etc. Measurements on a wide variety of such rubbers are being made, but such as have been completed suggest strongly that the method is generally applicable. For example, values of $8\left(\frac{t_r^{1/8}-1}{c}\right)$ for five different rubbers (see Table V) specially prepared at Sarnia for other work in this laboratory are plotted in Fig. 8.* The method seems to be as suitable for these as for normal GR-S rubbers. (It should be added that although the method has proved satisfactory for determining the value of the intrinsic viscosity of *whole* GR-S (in wide variety) in several solvents it has not been

TABLE V

SPECIAL GR-S – TYPE RUBBERS

(Prepared in Sarnia, Dec. 1945)

Charge No.	Modifier	Conversion, %	Mooney viscosity
P-443-1	*DDM*	73.3	45
B 1570	*DDM*	46.0	50
B 1569	*DDM*	71.6	46
B 1556	Tertiary C-14	75.5	45
B 1562	Sharples 3-B	75.2	50

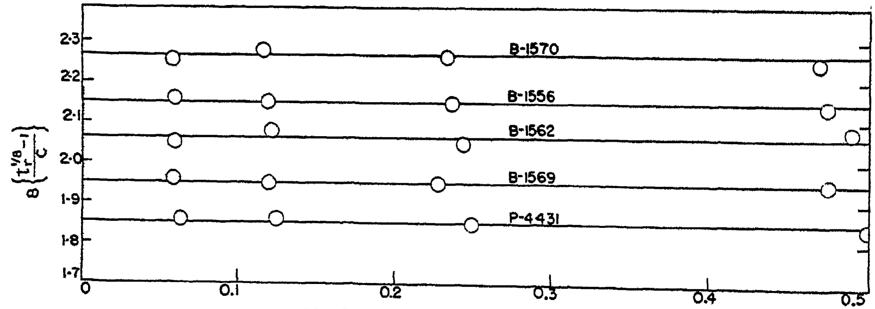

FIG. 8. *Variation of* $8\left(\frac{t_r^{1/8}-1}{c}\right)$ *with c, for five special rubbers.*

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* *As these rubbers contained some gel, the solutions were made by static extraction in the dark in a Baker cell, and the concentration of the undiluted solution was determined by evaporation of the solvent, from an aliquot sample, at 60° to 70° C. on a hot plate and finally in a vacuum oven.*

adequately tested for use with fractionated samples. Indeed there is evidence that with high or low molecular weight fractions a plot of $n\left(\frac{(t_r^{1/n} - 1)}{c}\right)$ against c does *not* give a horizontal line when $n = 8$; it does, however, give a straight line suitable for extrapolation, and a proper choice of n might restore the additional advantage of a zero slope.)

(4) *The Significance of n*

It has been pointed out by Huggins (21) and others, that viscosity–concentration equations containing an adjustable constant should give better agreement than inflexible equations such as those of Arrhenius or Philippoff. The value of such a constant depends on the nature of the solute and of the solvent and on the temperature, but is independent of molecular weight. Huggins showed (21) that many of these constants can be expressed in terms of the K' of Equation (2). Ewart (13, p. 211) pointed out that if the inherent viscosity is related to the concentration by the equation (27)

$$\frac{\ln \eta_r}{c} = [\eta] - \beta\,[\eta]^2\,c\,, \tag{12}$$

the constant β is related to K' by the expression $\beta = 0.50 - K'$.

By expanding the modified Baker Equation (5) binomially and neglecting higher terms in c, it may be shown that

$$K' = (n - 1)/2n$$
$$\text{and } \beta = 1/2n$$

Ewart emphasizes the importance of determining the value of K' or β; obviously the evaluation of n would be just as useful.

It is perhaps worth pointing out that in terms of K' or β there is very little difference between the values $n = 7$ and $n = 9$; the range $n = 8 \pm 1$ is equivalent to $K' = 0.437 \pm 0.008$ or to $\beta = 0.064 \pm 0.008$. To make it possible to make an unequivocal choice between $n = 7$ and $n = 8$, measurements would have to be precise enough to fix the $\frac{\ln t_r}{c}$ slope as $0.071\ [t]^2$ rather than $0.062\ [t]^2$. If $\frac{\ln t_r}{c}$ is to be independent of c, n must be infinite. If n is a finite number, the $\frac{\ln t_r}{c}$, c line cannot be horizontal, and its slope will increase with increasing molecular weight of the polymer.

(5) *The One-Point Determination of Intrinsic Flow Time*

For routine use there are very obvious advantages in a method by which intrinsic viscosity may be calculated from a single measurement of flow time. (For this purpose, certainly, $[t]$ and $[\eta]$ may be regarded as equivalent (3, 36).) Any viscosity–concentration function that reduces in the limit ($c \rightarrow 0$) to $[\eta]$ and is linear up to a concentration where precise measurement is possible could in principle be adapted to such a one-point determination. Nevertheless the function that is most frequently used in this way is the inherent viscosity, for, in general, it is much less dependent on c than the other functions commonly employed. The relative flow time is determined at a concentration such that t_r lies in the range 1.2 to 1.4 (15, 16, 17, 24), and $[\eta]$ is calculated as $\frac{\ln t_r}{c}$ (15).

It is evident, from Fig. 4 and from Table III, that the function $8\left(\frac{t_r^{1/8} - 1}{c}\right)$* would be more suitable than $\frac{\ln t_r}{c}$ for this purpose. It gives a value closer to the true (extrapolated) value than does $\frac{\ln t_r}{c}$ even in the range $t_r = 1.2 - 1.4$, where the latter is most precise, and, being independent of concentration over a wide range, it can be used at concentrations where t_r is a larger and therefore more precisely measurable quantity.

The two methods were put to a practical test by having five experimenters make independent measurements and compute $[t]$ using the two different functions. The results are given in Table VI. They should be compared with the value, $[t] = 2.09 \pm 0.01$, obtained by extrapolation.

TABLE VI

ONE-POINT DETERMINATIONS OF INTRINSIC FLOW TIME

Experimenter	Date of test	Concentration, gm. GR-S/100 ml. soln.	t_0, sec.	t, sec.	$8\left(\frac{t_r^{1/8} - 1}{c}\right)$	$\frac{\ln t_r}{c}$
S.Z.	Feb. 27	0.2371	171.1	276.3	2.08_5	2.02_2
S.Z.	Feb. 27	0.0813*	171.1	202.1	2.07_0	2.04_9
L.M.F.	Feb. 27	0.0790*	170.8	201.0	2.08_6	2.06_1
L.M.F.	Feb. 27	0.2733	170.8	297.2	2.09_8	2.02_7
D.A.H.	Feb. 28	0.2019	171.0	257.6	2.08_0	2.02_7
D.S.	Feb. 28	0.2043	171.0	260.2	2.11_0	2.05_2
P.B.S.	Feb. 28	0.2112	171.0	263.3	2.09_8	2.04_2

The apparatus and technique used were those already described. With one exception (P.B.S., whose values of t_0 and t were averages of readings obtained with only one filling of the viscometer) the values represent the mean of measurements with more than one filling. The precision in all cases was ± 0.1 sec. Each experimenter took his sample from a different portion of the 7 lb. bale.

It is noteworthy that with the proposed method all the values lie in the range 2.09 ± 0.02 (2.09 ± 1%). On the other hand, the values of the inherent flow time, $\frac{\ln t_r}{c}$, vary as much as 3½% from the 'correct' value. Even the determinations made in the recommended range (marked *) are in error by at least 1½%.*

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* *A function of this form, viz.* $\frac{8}{c}\left(\sqrt[8]{\eta_r} - 1\right)$, *has been used by Hess and Philippoff (19) and by Conrad (8).*

As these results were obtained by five different experimenters whose experience with this sort of measurement differed widely, and, as samples were taken at random, it seems reasonable to conclude that any well trained technician could obtain comparable results. In routine practice, therefore the intrinsic viscosity of whole GR-S may be more precisely determined as $8\left(\frac{t_r^{1/8}-1}{c}\right)$ than as $\ln t_r$

It might of course be argued that $\frac{\ln t_r}{c}$, or for that matter t_{sp}/c or $\log\frac{t_{sp}}{c}$, could give equally precise values of $[\eta]$ if the slope constant β (or K', or K) were determined once and for all for the given polymer–solvent system (as we have determined n). In each case, however, the slope term includes $[\eta]^2$ as well as the constant, so that calculation would have to be done by successive approximation. The desire to avoid such calculations doubtless accounts for the widespread preference for the use of $\frac{\ln t_r}{c}$ as an approximation of $[\eta]$.

It is evident, therefore, that $8\left(\frac{t_r^{1/8}-1}{c}\right)$ rather than $\frac{\ln t_r}{c}$ best combines convenience and precision for a one-point determination of intrinsic viscosity. The formula has been proved valid for a wide variety of rubbers of the GR-S type, and may be safely used with unfractionated normal GR-S. If, however, a rubber is known (or suspected) to differ markedly from normal GR-S, the formula should first be tested by determining t_r at several concentrations and plotting $8\left(\frac{t_r^{1/8}-1}{c}\right)$ against c.

With normal GR-S (for which $[\eta]$ is about 2) a suitable concentration is 0.25 gm. per 100 ml. solution; in general the concentration should be such that the value of t_r is between 1.4 and 2.2.

Acknowledgment

We wish to express our appreciation to the National Research Council of Canada for the Bursary granted to one of us (D. A. H.) and for financial support for the research received through the Associate Committee on Synthetic Rubber Research.

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* *This, of course, is what might be expected. If* $n = 8$, *the slope of the* $\frac{\ln t_r}{c}$, c *curve is* $-0.06_3\,[t]^2$. *Assuming no error in the determination of* $\frac{\ln t_r}{c}$ *at* $c = 0.08$ *(a very brave assumption indeed!) the error in the value of* $[t]$ *caused by supposing* $\frac{\ln t_r}{c}$ *to be independent of* c *is* $0.06_3 \times [t] \times 0.08 \times 100\%$ *or, when* $[t] = 2.1$, *1%. And, of course, when* $c = 0.3$, *where measurement is much more precise, this error is much larger, 4%.*

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A NOTE ON THE VARIATION WITH TEMPERATURE OF THE INTRINSIC VISCOSITY OF GR-S IN BENZENE[1]

By T. M. Rogers,[2] D. A. Henderson,[3] and L. H. Cragg[4]

Abstract

The intrinsic viscosity, $[\eta]$, (as well as the intrinsic flow time, $[t]$, and the intrinsic kinematic viscosity, $[\nu]$) of normal GR-S in benzene has been shown to be independent of temperature, over the range 10° to 55° C., within the experimental precision (± ½%). In this range of temperatures, also, the functions $8\,\dfrac{(t_r^{1/8}-1)}{c}$ and $8\,\dfrac{(\nu_r^{1/8}-1)}{c}$ are independent of concentration (up to at least 0.3%), and may therefore be used in the one-point determination of $[t]$ and $[\nu]$.

Introduction

The viscosity of a solution of a high polymeric substance is very sensitive to changes in temperature; but since the viscosity of the solvent is likewise sensitive, and in the same sense, the relative viscosity of the solution (i.e., its viscosity relative to that of the solvent) is much less dependent on the temperature. With some substances, such as cellulose and its derivatives, this temperature dependence is still considerable; with others, such as natural rubber, and many synthetic polymers (11; 12, pp. 203-220; 9; 13) it is relatively small.

The results obtained by different investigators with a given polymer, such as rubber (1, 7, 8, 11, 16), are often contradictory, but the discrepancies may be attributed to the fact that measurements were made in a variety of solvents and at different concentrations (7). Such discrepancies would of course be avoided if intrinsic viscosities were determined, in one solvent. Few careful studies of the variation of intrinsic viscosity with temperature have been reported—none, so far as we are aware, for the important system GR-S – benzene. Unpublished results* indicate that the intrinsic viscosity of GR-S in benzene or in toluene varies very little with temperature and that for practical purposes it may be determined at any convenient temperature between 20° and 30° C. Because it seemed important, for both practical and theoretical (2) reasons, to know more precisely the relation between $[\eta]$ and temperature, it was decided to determine it with the precision made possible by the use of the modified Baker equation (3, 5).

[1] *Manuscript received October 31, 1946.*

Contribution from the Department of Chemistry, McMaster University, Hamilton, Ont. The results here reported were given confidential circulation by the Associate Committee on Synthetic Rubber Research of the National Research Council of Canada in a report dated February 28, 1946.

[2] *Senior student.*

[3] *Graduate Student, holder of a Bursary under the National Research Council of Canada. Present address: Polymer Corporation, Sarnia, Ont.*

[4] *Assistant Professor of Chemistry.*

* *Private communications: F. T. Wall, June 19, 1944; P. J. Flory (et al.), Sept. 13, Dec. 22, 1943.*

Experimental

The apparatus and technique were essentially those described in a previous paper (5). Temperatures were maintained constant to ± 0.01° C., and even at 55° C. evaporation of the solvent during measurement was quite inappreciable. In all the experiments the solvent was benzene, purified as before (5).

A preliminary investigation was made using a sample of plant GR-S (obtained from Polymer Corporation, Sarnia, July 7, 1945) and a standard Ostwald–Cannon–Fenske viscometer A.S.T.M. No. 50. Determinations of relative flow time were made at one concentration at five temperatures ranging from 15° to 55° C. Since in the function intrinsic viscosity ($[\eta] \equiv \lim_{c \to 0} \frac{\ln \eta_r}{c}$) c is the concentration in grams per 100 ml. solution (4, 10), and therefore varies with the temperature, the solutions were prepared at the temperature of measurement (see Discussion). The results, shown in Table I and Fig. 1, indicate that $[t]$ varies linearly with temperature and is practically constant over the 40° C. range within which such measurements are usually made.

TABLE I

ONE-POINT DETERMINATION OF $[t]$ AT DIFFERENT TEMPERATURES

Conc'n., c (gm. GR-S per 100 ml. soln. at θ ° C.)	Temp., θ ° C.	Rel. flow time, t_r	$[t]$ dl./gm.
0.1500	15.05	1.358	2.08
0.1500	25.00	1.357	2.07
0.1500	35.00	1.356	2.07
0.1500	45.00	1.355	2.07
0.1500	55.00	1.352	2.06

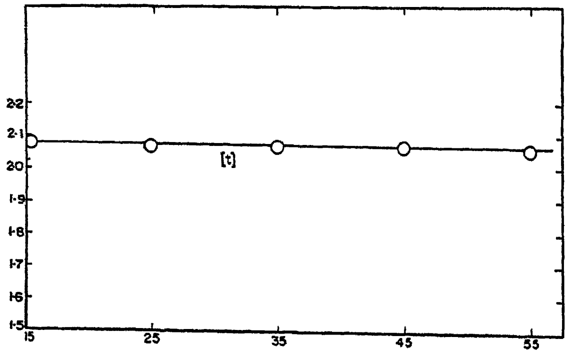

FIG. 1. *Variation of intrinsic flow time with temperature.*

Independent measurements were made with a different sample of GR-S and a different viscometer. The GR-S came from the same bale as that used in an earlier investigation (5); the dimensions of the viscometer have already been given in detail (5).

Two solutions of GR-S in benzene were prepared, of concentrations 0.3066 gm. per 100 ml. at 10.00° C. and 0.3010 gm. per 100 ml. at 50.00° C. These were successively diluted at the respective temperatures, giving six solutions in each series. The experimental data and the calculated values of the function $8\,\frac{(t_r^{1/8}-1)}{c}$ are given in Table II. From these, values of $[t]$ are readily obtained (with a precision of ± 0.01): 2.09 at 10° and 2.08 at 50° C. (see Fig. 2).

TABLE II

THE BAKER FUNCTIONS ($n = 8$) AT TWO TEMPERATURES

10.00° C.			50.00° C.		
Concentration, gm. GR-S/100 ml. soln.	$8\,\frac{(t_r^{1/8}-1)}{c}$	$8\,\frac{(\nu_r^{1/8}-1)}{c}$	Concentration, gm. GR-S/100 ml. soln.	$8\,\frac{(t_r^{1/8}-1)}{c}$	$8\,\frac{(\nu_r^{1/8}-1)}{c}$
0.3066	2.08	2.11	0.3010	2.08	2.11
0.2537	2.08	2.11	0.2500	2.07	2.10
0.2020	2.09	2.12	0.2035	2.09	2.11
0.1583	2.09	2.13	0.1550	2.08	2.10
0.1011	2.09	2.13	0.1071	2.09	2.12
0.0570	2.10	2.13	0.0559	2.09	2.12

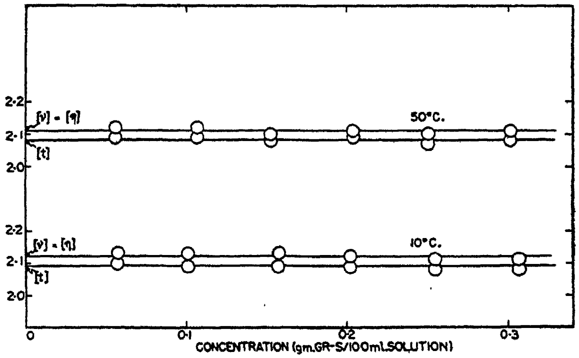

FIG. 2. *Variation of* $8\,\frac{t_r^{1/8}-1}{c}$ $\left(\textit{and } 8\,\frac{\nu_r^{1/8}-1}{c}\right)$ *with concentration at 10° and 50° C.*

To permit calculation of $[\nu]$ and $[\eta]$ from $[t]$, calibration constants for the viscometer and the rate of change of the density of the solutions with concentration must be known. From measurements of the viscosity of carefully purified water, benzene, toluene, and aniline at 25° C. the constants of the equation

$$\nu = At + B/t$$

were determined for this viscometer as follows: $A = 4.122 \times 10^{-5}$, $B = -1.9 \times 10^{-2}$. By means of this equation values of relative kinematic viscosity, ν_r, and of $8\,\frac{(\nu_r^{1/8} - 1)}{c}$ were calculated (Table II), and from them the values of $[\nu]$, 2.12 at 10°, and 2.11 at 50° C.

The intrinsic viscosity $[\eta]$ is theoretically not identical with $[\nu]$ (15), for if $\left(\frac{d\,\rho_r}{dc}\right)_{c\to 0} = \alpha$ (where ρ_r is the relative density of solution and solvent) then $[\eta] = [\nu] + \alpha$*. The densities of three solutions of GR-S in benzene (of concentrations 0.1203, 0.2478, and 0.4018 gm. per 100 ml. solution) were carefully determined at 25.00 ± 0.02° C. in a modified Sprengel pycnometer. Within the experimental error the relative density was a linear function of concentration:

$$\rho_r = 1 + 9 \times 10^{-4}\,c\ .$$

Hence, at 25° C., $[\eta] = [\nu] + 0.0009$. Since the precision of our values of $[\nu]$ is no better than ± ½%, it is quite safe to assume that within the experimental error $[\eta] = [\nu]$ at any temperature in the range 10° to 55° C.†

The values of $[t]$, $[\nu]$, and $[\eta]$ obtained for the GR-S – benzene system are listed in Table III.

TABLE III

TEMPERATURE DEPENDENCE OF THE INTRINSIC VISCOSITY FUNCTIONS (GR-S IN BENZENE)

Temp., ° C.	$[t]$	$[\nu]$, dl./gm.	$[\eta]$
10.00 (± 0.01)	2.09 (± 0.01)	2.12 (± 0.01)	2.12 (± 0.01)
25.00	2.09[1]	2.12	2.12
50.00	2.08	2.11	2.11

[1] *Value obtained, for the same sample of GR-S, in an earlier investigation (5).*

Discussion

From these results it may be concluded:

(1) That the function $8\,\frac{(t_r^{1/8} - 1)}{c}$ is independent of c at 10° and 50° C. as well as at 25° C. (5), and may therefore be used with confidence for the one-point determination of $[t]$ at any temperature in this range.

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* $\eta/\eta_0 = \nu\rho/\nu_0\rho_0$ or $\eta_r = \nu_r\,\rho_r$. Therefore

$$\left(\frac{d\,\eta_r}{dc}\right)_{c\to 0} = \left(\frac{d\,\nu_r}{dc}\right)_{c\to 0} + \left(\frac{d\,\rho_r}{dc}\right)_{c\to 0} \text{ or } [\eta] = [\nu] + \left(\frac{d\,\rho_r}{dc}\right)_{c\to 0} .$$

If $\rho = \rho_0\,(1 + \alpha\,c + \beta c^2 + \gamma c^3 + \ldots)$, then $\left(\frac{d\,\rho_r}{dc}\right)_{c\to 0} = \alpha$.

† *This is in agreement with the more general observation of Wagner (14) that the error produced in the inherent viscosity (and therefore in the intrinsic viscosity) by assuming that the densities of solvent and solution are equal probably never exceeds 0.01 of a unit.*

(2) That the intrinsic flow time, intrinsic kinematic viscosity, and intrinsic viscosity of GR-S in benzene are independent of temperature, within the experimental error, over the range 10° to 55° C. Any convenient temperature in this range may therefore be selected for viscosity determinations (provided of course that the temperature be the same for measurements with solvent and solution).

It should be emphasized that in this work c is the concentration in grams solute per 100 ml. solution, the volume being measured at the temperature at which viscosities are determined. As Philippoff points out (12, p. 168)

$$[\eta]_g = [\eta] \times \rho_0 ,$$

where ρ_0 is the density of the solvent, and $[\eta]_g$ is the function corresponding to $[\eta]$ when c is the concentration in grams solute per 100 gm. solution. In the work of Philippoff and of other investigators (particularly in Europe), it is the variation of $[\eta]_g$ with temperature that is usually determined. This has the advantage that viscosity measurements can be made on the same solution at the various temperatures; and $[\eta]$ can be calculated at each temperature from $[\eta]_g$ and ρ_0. In this investigation, however, $[\eta]$ was determined directly, in accordance with general practice on this continent. If values of $[\eta]_g$ are desired for purposes of comparison, they may be obtained from those of $[\eta]$. Thus, at 10° C. $[\eta]_g = 1.88$, at 50° C., 1.79 hgm. per gm.* For this system the density is, with sufficient precision for the present purpose, a linear function of temperature, and $[\eta]$ is constant; therefore, in range 10° to 55° C., $[\eta]_g$ is a linear function of temperature, and

$$\frac{\Delta\,[\eta]_g}{\Delta\,t} = \frac{\Delta\rho_0}{\Delta\,t}\,[\eta] = -\,1.06 \times 10^{-3}\,[\eta]\,.$$

The temperature independence of intrinsic viscosity of GR-S in benzene is not surprising when one considers the behaviour of related polymer–solvent systems. For example, Daneš (6) has shown that the intrinsic viscosity of styrene in benzene is almost independent of temperature over the range 15° to 65° C.; and the data of Whitby and Gallay (16) indicate that the intrinsic viscosity of natural rubber in benzene increases but very slightly with temperature.† As benzene is a 'good' solvent for these materials this behaviour is in accordance with theory (see, for example, Alfrey, Bartovics, and Mark (2)). It will be interesting to compare with that described here the behaviour of GR-S in other solvents, including 'poor' solvents and solvent – non-solvent mixtures; the necessary experiments are now in progress.

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* *Just as the units of $[\eta]$ are decilitres per gram (the reciprocal of grams per 100 ml.—see the letter to the Editor, J. Colloid Sci. 1, 465-466. 1946.), so the units of $[\eta]_g$ would be the reciprocal of grams per 100 gm., i.e., hectograms per gram.*

† *Values of $[\eta]$, calculated as $8\,(t_r^{1/8} - 1)/c$ (cf. Philippoff (11)), on the assumption that $\rho_r = 1.00$, are as follows; 4.0_6 at 11°, 4.2_0 at 25°, 4.2_9 at 35°, 4.2_9 at 40°, 4.3_3 at 45°, and 4.2_6 at 50° C.*

Acknowledgments

The authors wish to express their thanks to Mr. D. B. Sharpe for a careful and independent calibration of the viscometer, and to The National Research Council of Canada for financial support in the form of a Bursary (D. A. H.) and a grant, through its Associate Committee on Synthetic Rubber Research, in aid of the research.

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THE GROWTH OF La^{140} (40 hours) FROM Ba^{140} (12.7 days)[1]

BY W. E. GRUMMITT,[2] J. GUÉRON,[3] G. WILKINSON,[4] AND L. YAFFE[2]

Abstract

The composite self-weakening relations for La^{140} and Ba^{140} have been measured. Using these data, the growth of the La^{140} daughter from the Ba^{140} parent has been studied and compared with the growth calculated from the radioactive dependence laws. It is shown that, in the comparison of the activities of different β^- emitters, there is a danger in the use of corrections obtained by extrapolations of self-weakening and external absorption data.

The barium isotope, Ba^{140} of 12.7 days half-life, was first observed in the fission products of neutron-bombarded uranium by Hahn and Strassmann (4, 5). The isotope was identified as Ba^{140} owing to the growth of a 40 hr. lanthanum daughter activity identical as regards half-life and radiation characteristics with the La^{140} isotope formed by thermal neutron capture in lanthanum. The disintegration scheme for mass 140 is

$$Xe^{140}(16\text{ sec.}) \longrightarrow Cs^{140}(\text{short}) \longrightarrow Ba^{140}(12.7\text{ days}) \longrightarrow La^{140}\ (40\text{ hr.}) \longrightarrow Ce(\text{stable}).$$

In the course of quantitative measurements on the formation of Ba^{140} in fission, it was found necessary to examine the growth of La^{140} from its parent. For the initial experiments only radium–beryllium sources were available for irradiation. In later experiments pile-irradiated material was used and the specific activity of the samples was correspondingly higher. In subsequent experiments the percentage transmission of the β^- rays through the counter windows was investigated.

Experimental

The chemical separation of barium from uranium fission products was adapted from the procedure described by Hahn and Strassmann (6). Barium, strontium, and lanthanum carriers were added, after solution of neutron-bombarded uranium oxide, UO_2, in nitric acid, and the ice-cold solution saturated with hydrogen chloride. The precipitated barium chloride was dissolved in water. Strontium carrier and acetic acid were added, followed by $6N$ ammonium acetate solution. Barium was precipitated as chromate by dropwise addition of potassium chromate to the boiling solution.

The precipitated chromate was centrifuged, washed with hot dilute acetic acid, and dissolved in dilute hydrochloric acid. Strontium carrier was added,

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Contribution from the Montreal Laboratories of the National Research Council of Canada. The work described in this paper was completed and reported, October 31, 1944, but could not be released for publication at that time owing to security regulations. Issued now as N.R.C. No. 1566.

[2] *Present address, National Research Council, Chalk River, Ont.*

[3] *Present address, Commissariat à l'Energie Atomique, 41 Avenue Foch, Paris, France.*

[4] *Present address, Chemistry Dept., University of California, Berkeley, California, U.S.A.*

followed by acetic acid buffer solution, and barium reprecipitated as chromate. The chromate was dissolved in the minimum of dilute nitric acid, lanthanum carrier was added, and barium precipitated by addition of red fuming nitric acid to the ice-cold solution. The barium nitrate was washed with acetone, dissolved in water and reprecipitated. Two fuming nitric acid precipitations were adequate for more than 99.5% removal of lanthanum daughter activity. In some cases, barium was subsequently precipitated as sulphate.

For the high specific activity samples, a similar chemical procedure was followed. However, care was taken to keep all volumes at a minimum. The amounts of added carrier were small (1 mgm. barium) and the final nitrate precipitation was carried out in a total of 2 ml. of solution.

La^{140} was obtained from a previously separated Ba^{140} source which was in equilibrium with its daughter activity. The barium nitrate was dissolved in water, lanthanum carrier added, and lanthanum hydroxide precipitated. The hydroxide was dissolved, barium carrier added, and the precipitation repeated several times. Lanthanum was finally precipitated by hydrofluoric acid.

Measurements

The procedure used was similar to that described previously (1, 3). In order to correct for the self-weakening of the β^- rays, the activities of samples of increasing mass thickness were measured and an extrapolation was made to zero mass thickness. Six samples of varying weights were spread evenly with the aid of acetone, on circular aluminium trays of area 7.1 $cm.^2$ These were counted in rotation on three β^- particle counters of the end-on type with mica windows of area 7.1 $cm.^2$, and mass thickness 4.5 mgm. per $cm.^2$ The air gap between sample and window was equivalent to a mass of 1 mgm. per $cm.^2$

In view of the comparatively rapid growth of the 40 hr. lanthanum from the 12.7 day parent, it is impossible to measure directly the β^- ray self-weakening of the latter. The self-weakening of the combined barium and lanthanum activities was therefore measured at frequent intervals, starting immediately after chemical separation of barium until transient equilibrium between parent and daughter had been reached.

In the later experiments β^- samples of high specific activity (mass less than 1 microgram) were counted on an aluminium tray and on a thin mica source holder. The mica holder was constructed in such a manner as to reduce scattering of the β^- rays from the source holder into the counter. These samples were also counted using 200 mgm. per $cm.^2$ aluminium as a backing material.

The activity at zero time, i.e., the time of final separation of barium from its lanthanum daughter, was obtained through a short extrapolation over the first two hours, when one can safely assume the growth of La^{140} to be a linear function of time. It is to be noted that the experimental La/Ba activity ratio depends critically on this zero value.

The external absorption of the β^- rays of the Ba^{140} and La^{140} was measured by interposing aluminium screens of varying mass thickness between the sample and counter window. From a semilogarithmic plot of these data, $\epsilon_{1/2}$, the external absorption half-thickness was found. An extrapolation of the above line to zero mass thickness was used to obtain a correction for the absorption of β^- rays in the window.

Owing to anomalies observed, further experiments on the transmission of β^- rays were performed, and for this purpose a thin-window counter was constructed. This consisted of a vacuum desiccator containing an end-on counter from which the 4.5 mgm. per cm.^{2} duraluminium window had been removed and replaced by a 0.2 mgm. per cm.^{2} silver leaf window. High tension leads were brought in through holes drilled in the desiccator sides. The sample was placed 1 cm. below the window as before. Provision was made for moving an absorber into position between the sample and counter by means of a magnet.

In operation, the sample was placed in position and the desiccator was evacuated, simultaneously evacuating the unsealed counter. The whole assembly was then filled with ethanol and argon to pressures of 0.5 and 9.5 cm. of mercury respectively.

In addition to the above, some measurements were performed with no window in the counter. No spurious effects were observed in either case.

Results

(*a*) *Low Specific Activity Samples*

In Table I, Column 2, is given the composite self-weakening half-thickness $\eta_{1/2}$ at various times. In Fig. 1, $\eta_{1/2}$ is plotted as a function of the percentage of lanthanum counts present (see below) in the total activity. The composite curve was found to follow, at all times, the logarithmic law reported earlier (1) in the case of isolated activities.* The experimental results thus obtained give, by extrapolation, the self-weakening half-thickness of both the 12.7 day Ba^{140} and the 40 hr. La^{140}. The extrapolated value of $\eta_{1/2}$ for La^{140} in barium sulphate substrate, 165 mgm. per cm.^{2}, agrees well with the value measured directly, 157 mgm. per cm.^{2} for La^{140} in lanthanum fluoride substrate. The value for Ba^{140} in barium sulphate is then estimated to be 92.5 mgm. per cm.^{2}

The counts of Ba^{140} at zero time, and the composite count at various times were corrected to zero thickness of sample by use of the self-weakening data. To obtain Ba and La β^- activities, a correction was applied for absorption in the counter window, using the measured values $\epsilon_{1/2} = 41$ mgm. per cm.^{2} for Ba^{140} and 76 mgm. per cm.^{2} for La^{140}. The thinnest absorber used was 3 mgm. per cm.^{2} aluminium.

* *It is obvious that if both radiations in a given sample obey the self-weakening relations (3) log* $\frac{N_0}{N} = \delta W$ *and log* $\frac{M_0}{M} = \psi W$, *the composite radiation cannot obey a logarithmic weakening law. However in the present case at least, when the self-weakening coefficients* δ *and* ψ *are not widely different, the logarithmic law is followed within the limits of experimental error.*

The ratio of $(La^{140} + Ba^{140})_t$ activity at various times, t, to the Ba^{140} activity at zero time for a thick sample, corrected as above, is plotted in Fig. 2 as a function of time.

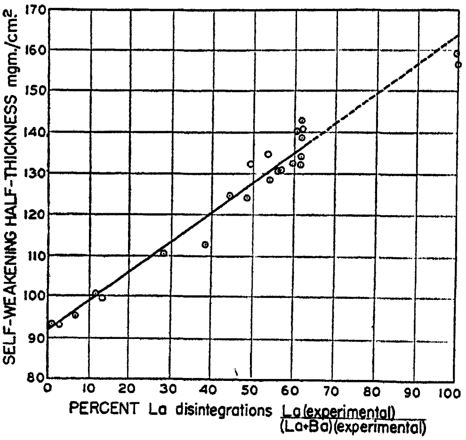

FIG. 1. *Composite* $(Ba^{140} + La^{140})$ β^- *ray self-weakening half-thickness vs. percentage* La^{140} *disintegrations.*

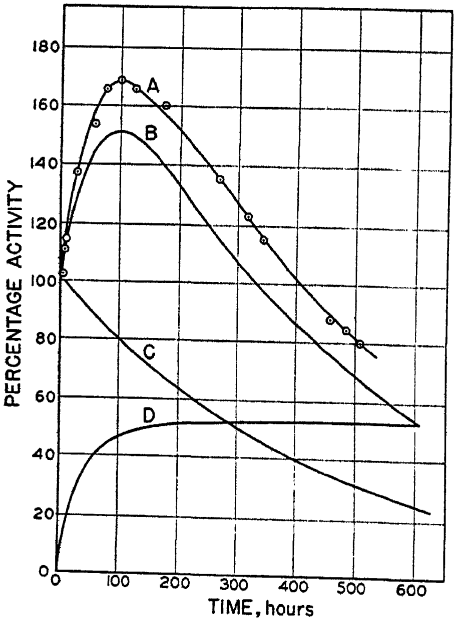

FIG. 2. *Experimental and theoretical growth and decay curves for* Ba^{140} *and* La^{140} β^- *activity.*

$A - \% \left\{\frac{(La + Ba)_t}{(Ba)_{t_0}}\right\}$ Experimental Thick sample

$B - \% \left\{\frac{(La + Ba)_t}{(Ba)_{t_0}}\right\}$ Theoretical

$C - \% \left\{\frac{Ba_t}{Ba_{t_0}}\right\}$ Theoretical

$D - \% \left\{\left(\frac{La}{La + Ba}\right)_t\right\}$ Theoretical

TABLE I

COMPOSITE SELF-WEAKENING AND Ba – La GROWTH DATA

Time, hr.	$\eta_{1/2}$ composite self-weakening half-thickness	Window correction applied from external absorption data				Window correction applied from 'windowless' counter experiments	
		$\frac{(Ba + La)_t}{(Ba)_{t_0}}$		α		Thin sample	
		Thick sample	Thin sample	Thick sample	Thin sample	$\frac{(Ba + La)_t}{(Ba)_{t_0}}$	α
0	93.9	100					
1.41	92.8	—					
1.67	93.8	102.68					
3.33	93.9	108.94					
5.00	95.4	111.43		1.38			
6.50	99.3	—					
6.67	100.6	114.31		1.33			
18.00	113.3	—					
24.37	110.6	137.66		1.26			
24.80	—	—	132.5		1.13	127.75	0.98
28.25	112.7	—					
45.00	119.7	—					
48.60	—	—	149.5		1.13	141.1	0.97
49.50	124.6	—					
53.40	124.8	153.82		1.17			
72.08	132.3	165.82		1.25			
72.30	—	—	156.0		1.13	146.6	0.97
76.50	124.6	—					
90.00	131.8	—					
96.50	128.2	—					
97.23	144.9	168.53		1.25			
121.23	140.8	—					
148.30	131.8	—					
170.00	—	—	148.9		1.13	137.4	0.97
173.15	142.4	160.16		1.30			
220.00	132.3	—					
264.55	140.8	135.23		1.32			
317.75	134.4	123.20		1.37			
341.12	139.4	115.15		1.33			
457.17	139.1	87.97		1.29			
480.27	139.2	84.99		1.33			
504.98	143.0	80.70		1.35			
				Average =1.30	Average =1.13		Average =0.97

The growth curve for the gross activity, calculated by the theory of successive radioactive decays (assuming one electron per disintegration for both β^- emitters) is given in Fig. 2, for comparison with the experimental curve, together with the calculated curves for Ba^{140} and $\frac{La^{140}}{(La^{140} + Ba^{140})}$.

The measured values of the activity ratio $\frac{(Ba^{140} + La^{140})_t}{(Ba^{140})_{t_0}}$ are given in Table I, for thick and thin samples, together with values of α, where α is the ratio of the measured lanthanum activity to the lanthanum activity calculated from the initial barium activity stated above.

The results of Fig. 2 and Table I show that, after application of the above corrections for absorption of β^- rays, the measured growth of La^{140} from its parent in a thick source appears to be in excess of the theoretical value by the factor $\alpha = 1.30$. The experimental transient equilibrium activity ratio $\frac{La^{140}}{Ba^{140}} = 1.47$, whilst the calculated value $= 1.16$.

(b) *High Specific Activity Samples*

The growth of La was observed in two very thin Ba samples (about 1 μgm. per cm.^{2}) with and without backing material. Corrections were applied as previously, with the exception that a self-weakening correction was not necessary in this case. In Table I, values of α for the experiments with backing material are given. With no backing material results for α are on the average about 5% lower.

(c) *Absorption of β^- rays in the Counter Windows*

It was found that when a 5 mgm. per cm.^{2} absorber was interposed between the very thin Ba^{140} sample and the thin window counter, the count was reduced to 80.5% of its former value. The result was similar when the thin window was removed. This is in contrast to an assumed value of 92% obtained by extrapolation of the external absorption, assuming, as usual, a logarithmic law, with the half-thickness of 41 mgm. per cm.^{2} as quoted above. In the case of the La β^- rays the absorption by the window was found to be substantially that predicted by the extrapolation, using the experimental half-thickness of 76 mgm. per cm.^{2}

Discussion

From the results in Fig. 2 and Table I the measured growth of La^{140} from its parent is apparently in excess of the theoretical value by the factor α when window corrections are made by the usual method. The experimental transient equilibrium activity ratio $\frac{La^{140}}{Ba^{140}}$ is considerably greater than the calculated value of 1.16.

Two interpretations of this observation might be proposed.

(1) That Ba^{140} emits one electron per disintegration to give its daughter La^{140}, which then emits 1.3 electrons per disintegration. This appears unlikely in view of β^- and γ-ray spectrometer measurements on La^{140} (2).

(2) That Ba^{140} gives only $\frac{1}{1.3}$ electrons observable in the counting arrangement used.

This second and more likely possibility would require that part of the Ba^{140} disintegrations proceed through a soft β^- particle emission. L. G. Elliott (2) has studied Ba^{140} with a β^- ray spectrometer and has shown β^- rays of maximum energy 1.03, 0.500, and 0.34 Mev., occurring respectively in 50, 25, and 25% of the disintegrations.

The predicted transmission of these electrons, based on a maximum energy – half-thickness relation for single energy β^- emitters, is 81% through a 5 mgm.

per cm.^{2} window, while the observed value is 80.5%. The relation obtained using aluminium absorbers in the present geometry is similar to that given by M. Perey (7). The above values are in contrast with a predicted transmission of 92% obtained from the usual extrapolation of external absorption data.

The discrepancies in α between the thick and thin samples indicate that an error is similarly introduced by the self-weakening corrections. A deviation from linearity over the initial portion of the logarithmic self-weakening relations would not have been noticed in the present measurements because (for intensity reasons) the thinnest sample measured had already a mass thickness of 20 mgm. per cm.^{2}

These observations show that in comparing the activities of different β^- emitters, there is a danger in the use of corrections obtained by extrapolation of self-weakening and external absorption data. Particularly in the case of emitters with complex spectra it is essential to use the thinnest possible samples both in actual measurements and in establishing the preliminary correction curves.

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THE FISSION YIELDS OF Ba^{139} AND Ba^{140} IN NEUTRON FISSION OF U^{235} AND U^{238} [1]

By W. E. Grummitt,[2] J. Guéron,[3] G. Wilkinson,[4] and L. Yaffe[2]

Abstract

The fission yields for Ba^{139} and Ba^{140} for thermal neutron fission of U^{235} and fast fission of U^{238} have been measured using naturally occurring uranium. This was accomplished by comparing the barium fission product activities with the U^{239} formed in radiative capture. With these data the fission yields were calculated from known values of the cross-sections for thermal fission and capture in uranium and were found to be 6.1% and 5.6% for Ba^{139} and Ba^{140}, respectively, for thermal fission and 5.1% and 4.2% for Ba^{139} and Ba^{140}, respectively, for fast fission. The contribution of resonance fission to the thermal neutron effect has been shown to be less than 5% in the irradiation arrangement used.

Introduction

Anderson, Fermi, and Grosse (1) introduced the concept of fission yields in the formation of fission products from uranium. The fission yield may be defined as the probability of a given isotope's being formed in fission.

$$\text{Fission yield} = \frac{\text{Number of fissions giving rise to the isotope}}{\text{Total number of fissions}}\,.$$

A determination of the fission yield of a given isotope requires the following data:

(*a*) The number of fissions occurring in a sample per unit time;

(*b*) The disintegration rate of the particular isotope in the sample at a steady state. This condition is usually referred to as 'saturation of bombardment'.

The direct measurement of the number of U^{235} thermal neutron fissions occurring in a uranium sample may be avoided if natural uranium is bombarded with thermal neutrons. In this case U^{238} undergoes radiative capture to form U^{239} (23.5 min.) whilst U^{235} undergoes thermal neutron fission. The β^- activities produced both by capture and by fission in natural uranium in thermal neutron bombardment are proportional to the respective cross-sections for these processes. Thus

$$\frac{\beta^-\text{ activity of }U^{239}\text{ at saturation of bombardment}}{\beta^-\text{ activity of fission isotope at saturation of bombardment}} = \frac{\sigma_c}{Y_f\cdot\sigma_f}\,,$$

where σ_c and σ_f are the respective capture and fission cross-sections for

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[2] *Present address, National Research Council, Chalk River, Ont.*

[3] *Present address, Commissariat à l'Energie Atomique, 41 Avenue Foch, Paris, France.*

[4] *Present address, Chemistry Department, University of California, Berkeley, California, U.S.A.*

thermal neutrons in natural uranium and Y_f is the fission yield of the isotope studied.

The fission yields of Ba^{139} (86 min.) and Ba^{140} (12.7 days) produced by thermal neutron reaction with the U^{235} component of natural uranium have been measured; using additional data, yields for fast neutron fission in U^{238} have been calculated.

Experimental

The data required were the β^- activities of U^{239}, Ba^{139}, and Ba^{140}. These activities were measured after chemical separation from bombarded uranium using the usual radiochemical technique of carriers. Thermal neutron values were obtained by difference between the activities formed in the irradiation of samples in aluminium and cadmium vessels.

(i) *Bombardments*

The aluminium bombardment vessel consisted of two concentric cylinders with a bottom on the outer compartment. The vessel was 12 cm. high and the diameters of inner and outer tubes were 2.5 and 4 cm. respectively. An identical cadmium vessel was provided with cadmium caps for both the inner and outer tubes. The annular space was filled with about 200 gm. uranium oxide, U_3O_8. Five curies of mixed radium-beryllium neutron sources were placed in the centre compartment, and the whole set in a paraffin block. The following irradiations were made:

(*a*) Aluminium vessel in paraffin,

(*b*) Cadmium vessel in paraffin,

(*c*) Cadmium vessel in air as far away as possible from hydrogenous material.

Irradiations of about two hours were made for the study of Ba^{139}, whilst for Ba^{140}, the irradiation time was several weeks.

(ii) *Chemical Procedures*

Before bombardment, the uranium was freed from most of the UX(Th^{234}) by ether extraction of a saturated solution of uranyl nitrate. The ether solution was washed with a small quantity of water, then water extracted. This extract was evaporated and ignited to uranium oxide, U_3O_8.

After bombardment, the oxide was dissolved in concentrated nitric acid (1 ml. per gm. U_3O_8). From the solution of total volume about 200 ml., a small sample was taken for measurement of the U^{239} activity.

(*a*) *U^{239} purification.*—The uranium was precipitated from the uranyl nitrate solution as sodium uranyl acetate by the procedure given previously (4). After short irradiations one precipitation reduced sufficiently the UX and fission product contamination. For long bombardments, two precipitations were required.

(*b*) *Barium purification.*—The separation of barium from uranium and other fission product activities has been described previously (7). Barium was precipitated finally as sulphate and was washed first with water, then with acetone.

(iii) *Measurements*

The β^- particle counters were of the end-on type, with windows of area 7.1 cm.^{2} and mass thickness 4.5 mgm. per cm.^{2} All samples were of a mass thickness between 30 and 100 mgm. per cm.^{2} and were spread evenly on circular aluminium trays of area 7.1 cm.^{2} They were counted under reproducible conditions using a uranium reference.

The measurement of U^{239} activities has been described previously (4). The activity of Ba^{139} was followed for about two half-lives ($\backsim$ 130 min.), beginning immediately after the final separation. The long lived Ba^{140} + La^{140} background was obtained by measurement of the samples 24 hr. later, after complete decay of the 86 min. Ba^{139} activity. Decay of the 12.7 day barium, and growth of its 40 hr. lanthanum daughter have to be considered not only for the assessment of the 12.7 day barium activity, but also as a correction to be applied to the measured decay of the 86 min. activity.

(iv) *Calculations*

Let N_2 be the measured count of (Ba^{140} + La^{140}) at time t_2, where t_2 is long enough to allow complete decay of Ba^{139} and is measured from the end of the irradiation. Similarily t_1 is the time at which the composite (Ba^{139} + Ba^{140} + La^{140}) activity is measured (t_1 = four hours).

Let a_1 and a_2 be the self-weakening corrections for (Ba^{140} + La^{140}) at times t_1 and t_2 respectively. The measurement of self-weakening has been given previously (3, 6, 7). If r_1 is the quantity $\frac{(Ba^{140} + La^{140})}{Ba^{140}_{t_p}}$ at time t_1, and r_2 is the corresponding value at time t_2, then $\frac{N_2\, a_2\, r_1}{a_1\, r_2}$ gives the actual number of counts due to (Ba^{140} + La^{140}) in the sample at time t_1. $Ba^{140}_{t_p}$ is the Ba^{140} activity at the time of precipitation of barium (t_p).

If now N_0 is the number of counts of Ba^{139} obtained by difference and corrected for decay to the end of irradiation (t_0), the fully corrected number of counts Ba^{139} per gram U_3O_8 is then

$$N_{Ba^{139}} = N_0 \cdot a \cdot b \cdot \frac{0.893\, W_c}{W_s} \cdot \frac{1}{W} \cdot \frac{1}{S},$$

where a = self-weakening correction for Ba^{139} in $BaSO_4$,

b = correction for absorption of rays of Ba^{139} in counter window and air gap,

W_s = weight of measured barium sulphate sample,

$0.893\, W_c$ = weight of barium nitrate carrier used, expressed as barium sulphate,

W = total weight of uranium oxide,

S = fraction of saturation activity of Ba^{139} reached during the irradiation.

Similarly, the fully corrected counts per gram U_3O_8 of Ba^{140} is

$$N_{Ba^{140}} = \frac{N_2}{r_2} \cdot a_2 \cdot d \cdot b \cdot \frac{0.893\, W_c}{W_s} \cdot \frac{1}{W} \cdot \frac{1}{S},$$

where d = correction for the β^- decay of Ba^{140} from the end of irradiation to the time t_p,

b = correction for the absorption of Ba^{140} β^- rays in the counter,

N_2, a_2, r_2, W_s, W_c, W, and S have the same significance as above.

Results

For each bombardment, the fully corrected β^- counts of Ba^{140}, Ba^{139}, and U^{239} were calculated. These were averaged and are given in Table I, as counts per gram U_3O_8 bombarded. Thermal neutron activities were obtained by subtraction of the respective activities obtained from bombardments in aluminium and cadmium. In Table II are given the ratios for thermal and fast neutron fission of Ba^{139}/Ba^{140}, and the ratios of the U^{239} to barium activities at saturation of bombardment.

TABLE I

ACTIVITY GIVEN AS COUNTS PER GRAM U_3O_8 (AVERAGE OF FOUR EXPERIMENTS)

Experiment	Ba^{139}	Ba^{140}	U^{239}
Al in paraffin	407	274	4861
Cd in paraffin	121	77	1766
Cd difference	286	197	3095
Cd in air	113	72	295

TABLE II

ACTIVITY RATIOS AND FISSION YIELDS

	Thermal neutron fission	Fast neutron fission
Ba^{139}/Ba^{140}	1.45 ± 0.10	1.57 ± 0.10
U^{239}/Ba^{139}	10.8 ± 0.7	
U^{239}/Ba^{140}	15.7 ± 0.8	
Fission yield Ba^{139}	6.1×10^{-2}	5.1×10^{-2}
n yield Ba^{140}	4.3×10^{-2}	3.2×10^{-2}

Fission Yields of Ba^{139} *and* Ba^{140}

The ratio $\frac{\sigma_c}{\sigma_f}$ is obtained from published values of σ_{abs} (2) and σ_f (8) through the relation $\frac{\sigma_{abs} - \sigma_f}{\sigma_f} = \frac{\sigma_c}{\sigma_f}$. Values given are $\sigma_{abs} = 5 \times 10^{-24}$ cm.^{2}, $\sigma_f = 3 \times 10^{-24}$ cm.^{2} and therefore $\frac{\sigma_c}{\sigma_f} = \frac{2}{3}$. From these the fission yields of Ba^{139} and Ba^{140} can be calculated from the expressions given in the introduction.

It should be noted that, using this method, knowledge of the absolute values of σ_c and σ_f is not necessary, since only their ratio is involved. Any change in published value of the ratio $\frac{\sigma_c}{\sigma_f}$ will alter the fission yield values by the same factor.

(*a*) The experimentally determined yields for thermal neutron fission of U^{235} are given in Table II. The early paper of Anderson, Fermi, and Grosse gave values of 6.4×10^{-2} and 8.4×10^{-2} for Ba^{139} and Ba^{140} respectively.

(*b*) Broda, Kowarski, and West (5) studied the relation between Ba^{139} formed in fission, and the actual fission counting rate. A value of 0.84 ± 0.03 was obtained for the ratio of the amount of Ba^{139} produced per fission of U^{238}, to the amount of Ba^{139} produced per fission of U^{235}. Using this value, the fission yield for Ba^{139} and the apparent yield for Ba^{140} formed in fast fission of U^{238} can be calculated. The values are

$$Ba^{139}, \quad Y_f^1 = 0.84 \times 6.1 \times 10^{-2} = 5.1 \times 10^{-2},$$

$$Ba^{140}, \quad Y_f^1 = \frac{5.1 \times 10^{-2}}{1.57} = 3.2 \times 10^{-2} .$$

Discussion

In a previous paper (7) the authors discussed the abnormal growth of La^{140} from Ba^{140} and showed that $\frac{\text{La experimental}}{\text{La theoretical}} = 1.3$ owing to the existence in the Ba^{140} radiation of soft electrons which escape detection in the counting arrangement used. Thus the fission yield for this isotope and also for its daughter La^{140} is $1.3 \times 4.3 \times 10^{-2} = 5.6 \times 10^{-2}$ for thermal neutron fission, and 4.2×10^{-2} for fast neutron fission.

The 12.7 day barium can be used as a reference for determinations of fission yields of other fission isotopes by activity comparison methods, i.e., by comparison of Ba^{140} and other separated fission-product activities produced in the same sample by neutron bombardment. It is to be noted, however, that if activity comparisons are made under the same experimental conditions as are used here in the measurement of the fission yield for Ba^{140}, the apparent fission yield of 4.3×10^{-2} must be used as a reference, and not the value for mass 140 of 5.6×10^{-2}.

Contribution of Resonance Fission

A maximum value for the amount of Ba^{139} and Ba^{140} produced by a resonance neutron fission process can be deduced. This is based on the comparison of irradiations in the cadmium vessel, with and without surrounding paraffin. In the first case:

(*a*) Barium activity produced in fission of uranium under cadmium with paraffin present,

F = activity due to fast neutrons,
r = activity due to resonance neutrons,
n_1 = total activity of barium.

$$F + r = n_1 . \qquad (1)$$

In the second case:

(*b*) Barium activity produced in fission of uranium under cadmium with hydrogenous material removed,

F^1 = activity due to fast neutrons,

$\frac{r}{\alpha}$ = activity due to resonance neutrons,

n_2 = total activity of barium.

$$F^1 + \frac{r}{\alpha} = n_2 \tag{2}$$

$F - F^1 = \phi$, where ϕ is always positive but small, because in the experimental arrangement used, it is unlikely that many neutrons are reflected back into the sample with energy above the fast neutron fission threshold. U^{239} activity can be used as a measure of the extent to which resonance neutrons are reduced by removal of paraffin, neglecting fast neutron capture. Although this procedure is far from being strictly valid, an error in α, as determined by this means, will not affect the order of magnitude of the results.

The irradiation under cadmium (Table I) gives the result,

$$\frac{U^{239} \text{ activity with paraffin}}{U^{239} \text{ activity without paraffin}} = 6 \approx \alpha$$

From the above definitions,

$$n_1 - n_2 - \phi = (F + r) - \left(F^1 + \frac{r}{\alpha}\right) - (F - F^1)$$

$$= 0.84r\,,$$

$$\text{whence } \frac{r}{n_1} = \frac{(n_1 - n_2) - \phi}{0.84\, n_1} = \frac{0.07 - \phi/n_1}{0.84} - 0.1\ .$$

Referring to the activity due to thermal neutron fission ($\sim 2n_1$), a maximum value of 0.05 is obtained for the ratio. This value is quite similar to the epicadmium $\frac{1}{v}$ 'tail' of thermal neutron detectors such as boron trifluoride chambers and manganese and dysprosium in a geometry comparable to the one used here. Under the experimental conditions used, therefore, resonance fission cannot contribute more than 5% of the thermal fission observed.

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FISSION YIELDS OF MASSES 131, 132, 134, AND 136 FORMED IN NEUTRON FISSION OF URANIUM[1]

By L. Yaffe[2] and C. E. Mackintosh[3]

Abstract

The ratio of I^{131} (8.0 days) to Ba^{140} has been determined in neutron fission of uranium and the fission yield of the former calculated to be 2.23×10^{-2} from the previously reported value for Ba^{140}. This in turn permits the estimation of fission yields for the 132, 134, and 136 fission chains, the relative abundance of which, together with that of 131, has been obtained by Thode. The ratio of 54 min. I to Ba^{139} has been determined. Using the previously reported value for the fission yield of Ba^{139}, that for the iodine was found to be 5.75×10^{-2}. A mass of 134 is assigned to the 54 min. I on the basis of Thode's data.

Introduction

In an early paper, Anderson, Fermi, and Grosse (1) introduced the concept of the fission yield of a mass chain, this being the fraction of fissions occurring in such a manner as to form that chain. It should be pointed out that in the determination of fission yields, the stable member of the chain will provide the most accurate results, since fission may occur in such a manner that the chain is entered at any point. Amongst others they determined the fission yields for the mass chain 131 produced in thermal fission. They also determined the yields for the unidentified mass chains which contained the 2.4 hr. and 54 min. iodine terms.

Broda (2) has separated I^{131} and I^{133} from the fast neutron fission products of both uranium and thorium. He determined the half-lives of these two isotopes as well as their β^-ray absorption.

There are several unidentified mass chains ending in stable Xe as reported by Seaborg (5):

$$\begin{array}{ccccccc}
\mathrm{Sb}^{>131} & \longrightarrow & \mathrm{Te}^{>131} & \longrightarrow & \mathrm{I}^{>131} & \longrightarrow & \mathrm{Xe}^{>131} \\
\text{10 min.} & & \text{43 min.} & & \text{54 min.} & & \text{Stable} \\
 & & \mathrm{I}^{?} & \longrightarrow & \mathrm{Xe}^{?} & & \\
 & & \text{1.8 min.} & & & & \\
\mathrm{Sb}^{>131} & \longrightarrow & \mathrm{Te}^{>131} & \longrightarrow & \mathrm{I}^{>131} & \longrightarrow & \mathrm{Xe}^{>131} \\
\text{5 min.} & & \text{77 hr.} & & \text{2.4 hr.} & & \text{Stable}
\end{array}$$

The relative quantities of the stable xenon isotopes of masses 131, 132, 134, and 136 formed in fission have been determined with high accuracy by Thode and Graham (6) in a mass spectrographic study. The Xe was extracted from uranium that had been exposed to a high intensity of both fast and slow neutrons.

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[2] *Present address, National Research Council, Atomic Energy Division, Chalk River, Ont.*

[3] *Present address, Atomic Energy Research Establishment, Harwell, England.*

In the present paper we report the fission yield of the 8.0 day I^{131}. From this, yields can be assigned to the 132, 134, and 136 chains using the relative values obtained by Thode, assuming that no appreciable amount of Xe^{131} is formed directly in fission.

The fission yield of the 54 min. I has also been determined by comparison with that of Ba^{139}, the value for which has been previously reported (4). This, by comparison with Thode's relative values, leads us to propose a mass of 134 for the first unidentified chain above.

Experimental

(a) I^{131}

Several hundred grams of uranium oxide (UO_3) was irradiated in paraffin blocks with neutrons from a Ra–Be source for about 10 days in both aluminium and cadmium containers, as previously described (4). The source strength was kept constant for each set of experiments, but varied from 4 to 6 gm. radium from set to set.

The irradiated uranium oxide was well mixed and divided into two equal parts. Ba^{140} was extracted from one of these using the method previously described (3), and left to decay for 24 hr. to eliminate Ba^{139}, appropriate corrections being made for the growth of La^{140}.

From the second portion iodine was extracted as follows.

To the uranium oxide was added 100 mgm. potassium iodide as carrier. The mixture was then dissolved under reflux in sulphuric acid into which sulphur dioxide was bubbled constantly. After dissolution and cooling, the iodine was liberated with acidified sodium nitrite solution and extracted with carbon tetrachloride. The iodine solution in carbon tetrachloride was shaken with bromine water, and then with sodium nitrite solution to ensure against any loss of iodine. This operation was found necessary to remove traces of active bromine and was repeated three times, using fresh bromine water each time. The iodine solution was then reduced with sulphur dioxide water, reoxidized with sodium nitrite, reduced again, and copper iodide precipitated in presence of excess sulphur dioxide. The precipitate was washed with sulphur dioxide water and acetone, and then counted on paraffin-coated copper trays, using 'end-on counters'. The mica windows were 7.1 cm.^{2} in area and of mass thickness 4.5 mgm. per cm.^{2} The extraction yield was usually 75 to 80%.

The self-weakening and external absorption determinations were carried out on samples prepared in the same way. These data are given in Table I.

(b) *54 Min. Iodine*

The samples were irradiated in paraffin as in the case of I^{131}, but for 20 min. only. In addition some samples were also irradiated in graphite, using In to monitor the (X, n) source.

TABLE I

SELF-WEAKENING AND EXTERNAL ABSORPTION IN Al FOR I^{131} AND I (54 MIN.) IN COPPER IODIDE SUBSTRATE

Isotope	I^{131}	I[1] (54 min.)
Self-weakening half-thickness, $\eta_{1/2}$, mgm. per cm.^{2}	56 ± 6	151 ± 8
External absorption half-thickness, $\epsilon_{1/2}$, mgm. per cm.^{2}	22 ± 2	98 ± 4

[1] *This is one of the few instances in which the ratio* $\frac{\eta_{1/2}}{\epsilon_{1/2}}$ *is very different from 2.2. These values were checked repeatedly with consistent results.*

The counting technique was the same as above. However, both iodine and barium samples were counted immediately after purification.

The chemical extraction was the same as used for I^{131}.

(*c*) *Barium*

The activity of the I^{131} was compared with that of Ba^{140} and that of the 54 min. iodine with that of Ba^{139}, both barium activities being determined using aliquots of the various irradiated samples. In a previous paper (3) it was found that the fission yield for Ba^{140} was less than that indicated by studying the growth of the La^{140} daughter; this was due to a soft electron emission which was not counted in our arrangement. It should be noted that the fission yield for Ba^{140} which must be used for comparison purposes is the value experimentally obtained without correction, rather than the value determined from the growth of the La^{140} daughter.

Results

Table I gives the self-weakening and external absorption data for I^{131} and 54 min. I. The activities found in Ba^{140}, I^{131}, Ba^{139}, and 54 min. I are shown in Tables II and III. The fission yields of the two iodines are given, having been obtained from the Ba data. Table IV gives the fission yields of masses 131, 132, 134, and 136 calculated from the data of Thode (6) with reference to I^{131}. In Table V are shown the properties of the I fission fragments.

The activities found in Ba^{140}, I^{131}, Ba^{139}, and 54 min. I are given below in Tables II and III as counts per gram uranium oxide irradiated.

Discussion

The difference in fission yields for masses 131 and 134 between fast and slow fission is so small, and the accuracy of our measurements is of such an order, that it is possible to neglect the fact that a relatively considerable portion of fast fissions must have occurred in the metal studied by Thode. A comparison of Tables III and IV would indicate that a mass number of 134 can be assigned to the 54 min. iodine. It should be pointed out that this will be true whatever the absolute value set for the Ba^{139}, Ba^{140}, and I^{131} fission yields.

TABLE II

Fission yields of I^{131}[1]

Isotope	Trial 1, counts/min.	Trial 2, counts/min.	Fission yields, $\times 10^{-2}$	Remarks
Ba^{140}	145	142	4.3 (4)	
I^{131}	73	76	2.23 ± .11	Thermal neutrons
Ba^{140}	31	31	3.2 (4)	
I^{131}	23	21	2.27 ± .11	Fast neutrons

[1] *All data were corrected for self-weakening, absorption by the counter window and air gap, saturation of bombardment, decay, and for percentage recovery.*

TABLE III

Fission yields of 54 min. iodine[1]

Isotope	Graphite[2]		Paraffin		Remarks
	Counts/min. (average of two results)	Fission yield, $\times 10^{-2}$	Counts/min. (average of two results)	Fission yield, $\times 10^{-2}$	
Ba^{139}	2088	6.1 (4)	500	6.1 (4)	
$I^?$	1987	5.80 ± .10	466	5.70 ± .25	Thermal neutrons
Ba^{139}	79	5.1 (4)	167	5.1 (4)	
$I^?$	98	6.32 ± .12	173	5.28 ± .23	Fast neutrons

[1] *All data were corrected for self-weakening, absorption by the counter window and air gap, saturation of bombardment, decay, and for percentage recovery.*

[2] *Corrections were also made for variations in source intensity as monitored by In.*

TABLE IV

Fission yields calculated from xenon data of Thode and Graham (6) and fission yield of I^{131} (2.23%)

Mass number	Relative abundance (6)	Fission yields, (calc.) $\times 10^{-2}$
131	13.7	(2.23)
132	20.4	3.31
134	36.0	5.85
136	29.8	4.85

The following Table V gives a summary of the properties of the iodine fission fragments as they now appear to us, according to the above experiments.

TABLE V

PROPERTIES OF IODINE FISSION FRAGMENTS

Mass	Half-life	$\epsilon_{1/2}$, mgm./cm.^{2}	$\eta_{1/2}$, mgm./cm.^{2}	Fission yield, $\times 10^{-2}$		
				This report	Thode	Fermi *et al.*
129	Quite long[1]	—	—	—	—	—
131	8.0 days	22	56	2.23	2.23[2]	1.6
132	2.4 hr.	—	—	—	3.31	5.2
133	22 hr.	42 (2)	100 (2)	—	—	—
134	54 min.	98	151	5.75	5.85	12.0
135	6.6 hr.	—	—	—	—	—
136	1.8 min.	—	—	—	4.85	—

[1] *This may be inferred because*
(*a*). *Its activity has not been detected, while* Te^{129} *is known to be* β^-*-active, and* Xe^{129} *is stable, and,*
(*b*). *Thode has not found in fission Xe the mass 129 with an abundance high enough to account for the complete decay of* Te^{129} *(half-life 72 min. and a 32-day isomer).*

[2] *Reference fission yield.*

Acknowledgment

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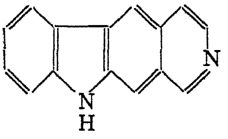
THE SYNTHESIS OF SOME CARBAZOLE DERIVATIVES[1]

By Richard H. F. Manske[2] and Marshall Kulka[3]

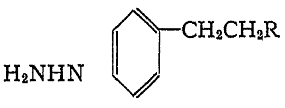
Abstract

In attempts to synthesize 10-pyrido(3,4-*b*)carbazole, a number of new compounds were prepared. These are β-(5,6,7,8-tetrahydro-3-carbazolyl)propionic acid, β-(5,6,7,8-tetrahydro-3-carbazolyl)ethylamine and their intermediates.

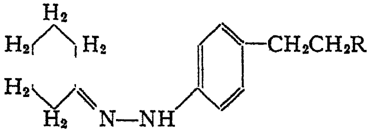
The compound, 10-pyrido(3,4-*b*)carbazole (I), does not appear to have been described. It was needed in connection with another problem and attempts were made to prepare it. Thus far, success has not attended these efforts but a number of new compounds of interest in themselves were synthesized and these are now described.



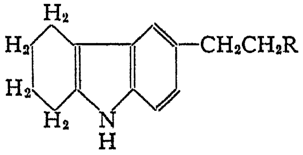
I



II (R = —COOH)
V (R = —N(CO)$_2$C$_6$H$_4$)



III (R = -COOH)
VI (R = -N(CO)$_2$C$_6$H$_4$)



IV (R = —COOH)
VII (R = —N(CO)$_2$C$_6$H$_4$)
VIII (R = —NH$_2$)

When 4-hydrazino-β-phenylpropionic acid (II) was condensed with cyclohexanone and the resulting phenylhydrazone (III) subjected to the Fischer indole ring closure a good yield of β-(5,6,7,8-tetrahydro-3-carbazolyl)propionic acid (IV) was obtained. In an attempt to convert (IV) to β-(5,6,7,8-tetrahydro-3-carbazolyl)ethylamine (VIII), the urethane of IV was prepared via the hydrazide, azide, and isocyanate successively and the urethane was fused with phthalic anhydride. The resulting oily material was not the required β-(5,6,7,8-tetrahydro-3-carbazolyl)ethylphthalimide (VII) since it did not produce any acid-soluble material when subjected to hydrolysis, according to the method of Ing and Manske (5). (VIII) was ultimately obtained from β-(4-hydrazinophenyl)ethylphthalimide (V) via its condensation with cyclohexanone, Fischer indole ring closure of the resulting (VI), and hydrolysis of the phthalimide (VII).

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Contribution from the Research Laboratories, Dominion Rubber Company Limited, Guelph, Ont.

[2] *Research Director.*

[3] *Research Chemist.*

Attempts to effect ring closure of the N-formyl, N-carbethoxy, and N-acetyl derivatives of (VIII) by means of phosphorus oxychloride failed. The tetrahydrocarbazole derivatives (IV) and (VII) could not be dehydrogenated under the conditions used. When heated at 230° C. with platinum oxide (VII) was recovered unchanged while (IV) yielded neutral material.

Experimental

p-Nitrohydrocinnamic Acid (1)

To a stirred solution of hydrocinnamic acid (200 gm.) in glacial acetic acid (100 cc.) was added dropwise fuming nitric acid (400 gm.) over a period of one hour. The temperature of the reaction mixture was maintained at 20° to 25° C. by means of a cold water bath. The reaction mixture was allowed to stand at room temperature for three hours with occasional cooling at first, and then poured into one litre of cold water. The yellow solid was filtered, washed with water, and recrystallized from ethanol. The yield of light-yellow needles was 94.5 gm. or 37%; m.p. 164° to 165° C.*

p-Aminohydrocinnamic Acid (3)

A hot solution of *p*-nitrohydrocinnamic acid (20 gm.) in 4 *N* ammonium hydroxide (100 cc.) was added to a boiling solution of ferrous sulphate heptahydrate (200 gm.) in water (400 cc.). The reaction mixture was treated with concentrated ammonium hydroxide until strongly alkaline, boiled for three minutes, more ammonium hydroxide (10 cc.) added, and the boiling continued for another two minutes. The black precipitate was filtered off under suction, the hot filtrate concentrated to about 250 cc., treated with charcoal, and filtered again. The filtrate on acidification with acetic acid and on cooling deposited white needle-like crystals (15.2 gm. or 90%), m.p. 131° to 132° C.

p-Hydrazinohydrocinnamic Acid (II)

To a solution of *p*-aminohydrocinnamic acid (28.0 gm.) in concentrated hydrochloric acid (45 cc.) and water (100 cc.) cooled below 0° C. was added a cold solution of sodium nitrite (11.0 gm.) in water (35 cc.) over a period of 10 min., the temperature of the reaction mixture being kept below 0° C. The resulting diazonium salt solution was added as quickly as possible to a chilled solution of sodium sulphite (110 gm.) in water (200 cc.). The amber solution was allowed to warm up gradually to room temperature, heated at 75° to 80° C. for three hours, acidified strongly with concentrated hydrochloric acid, heated for a further five hours, and cooled. The precipitated hydrazine hydrochloride was filtered, dissolved in a minimum amount of hot water, made alkaline with concentrated ammonium hydroxide, and adjusted to pH 5 with acetic acid. The precipitated hydrazine (23 gm. or 75%) was filtered off from the cooled solution, washed with a little cold water and dried, m.p. 158°

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* *All melting points are corrected.*

to 160° C. (decomposition), recrystallized from ethanol, m.p. 158° to 160° C. (decomposition). Calc. for $C_9H_{12}O_2N_2$: C, 60.00; H, 6.72; N, 15.56%. Found: C, 60.28, 60.37; H, 6.72, 6.57; N, 15.72, 15.53%.

Hydrazone of p-Hydrazinohydrocinnamic Acid and Cyclohexanone (III)

To *p*-hydrazinohydrocinnamic acid (23 gm.) dissolved in ethanol (350 cc.) was added cyclohexanone (11.0 gm.) and the resulting solution heated under reflux for five hours. The solution on concentration to about 200 cc. and cooling yielded yellow-orange needles (25 gm. or 75%) melting at 156° to 158° C. with decomposition. Calc. for $C_{15}H_{20}O_2N_2$: C, 69.20; H, 7.75; N, 10.76%. Found: C, 69.29, 69.21; H, 7.57, 7.86; N, 10.83, 10.93%.

β-(5,6,7,8-Tetrahydro-3-Carbazolyl)propionic Acid (IV)

The hydrazone of *p*-hydrazinohydrocinnamic acid and cyclohexanone (III) (8.8 gm.) was ground up to a fine powder and added to 17% by weight sulphuric acid (90 cc.) previously warmed up to 50° C. Most of the fine powder dissolved, and after a few minutes' stirring, a precipitate began to appear. The reaction mixture was heated on a water-bath at 65° to 70° C. for one hour, cooled, and the precipitate filtered and washed with water. Crystallization from methanol containing a little water yielded white needles (5.7 gm. or 70%), m.p. 118° to 120° C. Calc. for $C_{15}H_{17}O_2N$: C, 74.04; H, 7.05; N, 5.76%. Found: C, 74.02, 73.82; H, 7.19, 6.94; N, 5.76, 5.94%.

Methyl β-(5,6,7,8-Tetrahydro-3-Carbazolyl)propionate

To β-(5,6,7,8-tetrahydro-3-carbazolyl)propionic acid (3.5 gm.) dissolved in methanol (70 cc.) was added (1.8 gm.) concentrated sulphuric acid and the solution heated under reflux for six hours. To the cooled solution was added sodium bicarbonate (4 gm.) dissolved in water (30 cc.) and the methanol removed under reduced pressure. The precipitated ester (3.4 gm. or 92%) was filtered, washed with water, and dried, m.p. 76° to 78° C.; recrystallized from methanol–water m.p. 76° to 78° C. Calc. for $C_{16}H_{19}O_2N$: C, 74.71; H, 7.39; N, 5.32%. Found: C, 74.40, 74.50; H, 7.17, 7.20; N, 5.44, 5.46%.

β-(5,6,7,8-Tetrahydro-3-Carbazolyl)propionic Hydrazide

A solution of methyl β-(5,6,7,8-tetrahydro-3-carbazolyl)propionate (1.0 gm.), methanol (3 cc.) and hydrazine hydrate (1.5 cc.) was heated on the steam-bath, the methanol being allowed to distil off. After five hours' heating (0.5 cc.) more of hydrazine hydrate was added and the heating continued for another hour. The precipitated white solid (1.1 gm.) was filtered, washed with water, and dried. Recrystallization from ethyl acetate yielded yellowish microscopic crystals, m.p. 159° to 160° C. Calc. for $C_{15}H_{19}N_3O$: C, 70.04; H, 7.39; N, 16.34%. Found: C, 69.51, 69.35; H, 7.35, 7.25; N, 16.45, 16.12%.

β-Phenylethylphthalimide

This was prepared by fusing β-phenylethylamine (2) with phthalic anhydride. It had the same melting point as that reported in the literature (5).

β-p-Nitrophenylethylphthalimide

To stirred fuming nitric acid (*d.*, 1.5, 210 cc.) was added β-phenylethylphthalimide (85 gm.) over a period of 30 min., the temperature of the reaction mixture being kept at 20° to 25° C. by cooling. After allowing the reaction mixture to stand at room temperature for five hours, it was poured into cold water. The yellow precipitate was filtered, washed well with water, and dried. Two successive crystallizations from benzene yielded stout light-yellow needles (49 gm. or 50%) melting at 203° to 204° C. Calc. for $C_{10}H_{12}O_4N_2$: C, 64.86; H, 4.05; N, 9.46%. Found: C, 65.05, 64.92; H, 4.18, 4.12; N, 9.65, 9.53%. This compound when mixed with that obtained by fusion of *p*-nitrophenylethylamine (4) with phthalic anhydride gave no melting point depression.

β-p-Aminophenylethylphthalimide

A suspension of β-*p*-nitrophenylethylphthalimide (25 gm.) in ethanol (150 cc.) and 0.3 gm. of Adams platinum catalyst, was heated at 35° C. and shaken under an initial pressure of 40 lb. of hydrogen for 24 hr. Then the temperature was raised to 60° C. and the hydrogenation continued for another six hours, at the end of which time reaction was complete. To the reaction mixture about 250 cc. ethanol was added, and the whole heated until all the organic material dissolved, and then filtered. On cooling, the filtrate deposited yellow prisms (18.6 gm. or 83%) in two successive crops, m.p. 155° to 156° C., recrystallized from ethanol, m.p. 156° to 157° C. Calc. for $C_{16}H_{14}O_2N_2$: C, 72.18; H, 5.26; N, 10.53%. Found: C, 72.33, 72.37; H, 5.24, 5.06; N, 10.67, 10.73%.

β-p-Hydrazinophenylethylphthalimide (V)

β-*p*-Aminophenylethylphthalimide (5.0 gm.) was dissolved in hot water (150 cc.) containing concentrated hydrochloric acid (3 cc.), cooled, and to this was added concentrated hydrochloric acid (150 cc.). The reaction mixture was diazotized with a solution of sodium nitrite (1.30 gm.) in water (25 cc.), the temperature being kept below 0° C. After standing at 2° C. for eight hours, the reaction mixture was filtered to remove a small amount of undissolved material and the filtrate added as quickly as possible to a chilled solution of pure stannous chloride dihydrate (20 gm.) in concentrated hydrochloric acid (40 cc.). A white precipitate appeared immediately. The reaction mixture was allowed to stand at room temperature overnight and then filtered. The white solid was extracted with hot water (about 500 cc.) until no more dissolved, the extract treated with charcoal, filtered, and the hot filtrate basified with concentrated ammonium hydroxide and cooled. The yellow precipitate was filtered and recrystallized from ethanol, m.p. 165° to 166° C., yield 2.7 gm. or 50%. Calc. for $C_{16}H_{15}O_2N_2$: C, 68.33; H, 5.34; N, 14.95%. Found: C, 68.93, 68.75; H, 5.53, 5.54; N, 14.74, 14.98%.

Hydrazone of β-p-Hydrazinophenylethylphthalimide and Cyclohexanone (VI)

β-*p*-Hydrazinophenylethylphthalimide (4.0 gm.) was dissolved in hot ethanol (150 cc.), cyclohexanone (1.4 cc.) added, and the solution heated under reflux for one-half hour. The yellow precipitate was filtered off from the cooled solution, washed, and dried; yield 4.7 gm. or 90%, m.p. 181° to 183° C. with decomposition. Recrystallization from ethanol gave golden-yellow needles, m.p. 181° to 183° C. with decomposition. Calc. for $C_{22}H_{23}O_2N_3$: C, 73.13; H, 6.37; N, 11.63%. Found: C, 72.94, 72.97; H, 6.51, 6.37; N, 11.78, 11.51%.

β-(5,6,7,8-Tetrahydro-3-carbazolyl) ethylphthalimide (VII)

The hydrazone of β-*p*-hydrazinophenylethylphthalimide (6.2 gm.) (VI) was added to 17% by weight sulphuric acid (125 cc.) and heated on the steam-bath for one and a quarter hours with occasional stirring. The reaction mixture was diluted with water, filtered, washed, and dried. Recrystallization from ethanol yielded yellow needles (5.02 gm. or 85%) melting at 219° to 221° C.; recrystallized from ethyl acetate, m.p. 221° to 222° C. Calc. for $C_{22}H_{20}O_2N_2$: C, 76.74; H, 5.86; N, 8.14%. Found: C, 76.51, 76.53; H, 5.78, 5.89; N, 8.32, 8.32%.

β-(5,6,7,8-Tetrahydro-3-Carbazolyl) ethylamine (VIII)

To a solution of β-(5,6,7,8-tetrahydro-3-carbazolyl)ethylphthalimide (3.5 gm.) in ethanol (100 cc.) was added hydrazine hydrate (7 cc.) and the solution heated under reflux for one-half hour. To the cooled solution concentrated hydrochloric acid (35 cc.) was added and the resulting solution heated to boiling and then taken almost to dryness under reduced pressure. To the residue water was added, and the white insoluble phthalylhydrazide was filtered and washed with dilute hydrochloric acid. The combined filtrate and washings were basified with sodium hydroxide and extracted with ether. Removal of the ether yielded a yellow oil (1.75 gm. or 80%) which distilled at about 220° C. (2 mm.). It would not crystallize on cooling and scratching. Calc. for $C_{14}H_{18}N_2$: C, 78.45; H, 8.42%. Found: C, 78.12, 78.01; H, 8.35, 8.30%. This amine when heated with phthalic anhydride at 230° C. for a few minutes yielded a compound melting at 219° to 222° C., which did not depress the melting point of β-(5,6,7,8-tetrahydro-3-carbazolyl)ethylphthalimide (VII).

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THE PREPARATION, PURIFICATION, PHYSICAL PROPERTIES AND HYDROLYSIS OF CYANOGEN CHLORIDE[1]

D. E. Douglas[2] and C. A. Winkler[3]

Abstract

Cyanogen chloride, prepared by the method of Jennings and Scott, has been fractionally recrystallized to a constant freezing point of −6.90° C. Vapour pressure values for material purified in this way are in good agreement with the data of Klemenc and Wagner. The activation energy for the hydrolysis of cyanogen chloride at pH 4 to 6 between 0° and 50° C. is approximately 21 kcal. per mole.

This paper deals with the preparation, purification, and some physical properties of cyanogen chloride, together with a note on its hydrolysis in aqueous solution.

Experimental

Preparation and Purification of Cyanogen Chloride

Cyanogen chloride was prepared by the method of Jennings and Scott (2) from 200 gm. of sodium cyanide conditioned to approximately 2% moisture, and suspended in 300 ml. carbon tetrachloride. Chlorine was passed into this mixture for 8 to 12 hr., at such a rate that the temperature did not rise above 0° C. Efficient cooling and stirring of the reaction mixture were necessary, and care had to be taken that all the sodium cyanide had reacted before the passage of chlorine was stopped and distillation begun, otherwise loss of cyanogen chloride took place through reaction with sodium cyanide to form a black solid. The reaction vessel was cooled in an ice–salt bath, and the contents was stirred mechanically.

When the reaction was judged to be complete, a fractionating column and calcium chloride drying tube were fitted to the reaction flask, which was warmed to 15° to 20° C. by means of a water-bath that could be heated near the end of the distillation. In early preparations, the fractionating column was a water-jacketed condenser, the inner tube of which was packed with a series of glass disks, and about which water at 13° to 14° C. was circulated, but later, a simple tube about 18 in. long filled with copper gauze was employed with satisfactory results. The gaseous cyanogen chloride was condensed, after passing through the fractionating column and calcium chloride tube, in a trap or large ampoule immersed in an ice-bath. Distillation was stopped when the temperature in the reaction flask rose to 40° C. If the distillate contained free chlorine, as indicated by a greenish colour, mercury was added to the liquid, and it was shaken occasionally. The cyanogen chloride was distilled off from the residue.

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Contribution from the Physical Chemistry Laboratory, McGill University, Montreal, Que.

[2] *Demonstrator in Chemistry. Present address: Montreal General Hospital, Montreal, Que.*

[3] *Professor of Chemistry.*

Several methods of purifying cyanogen chloride reported in the literature were tried without success. Fractional distillation at reduced pressure at −78° C. did not remove the last traces of chlorine, and distillation through a suspension of zinc oxide and calcium carbonate caused a lowering of the freezing point of a fairly pure sample of cyanogen chloride. Chlorine was not removed satisfactorily by arsenic, antimony, or zinc metal. The material was finally purified by fractional crystallization of the distillate from the Jennings and Scott preparation.

The water-white distillate was frozen in the trap or ampoule used as a receiver, until it was 80 to 90% solid. The mother liquor was poured off, the solid remelted, and crystallization was repeated until no further rise in the freezing point occurred. In a typical purification, the freezing point rose from −7.73° C. after the first crystallization to a constant value of −6.90° C. after the third recrystallization. Usually three recrystallizations of redistilled cyanogen chloride were sufficient to give a product better than 99.5% pure.

Determination of Purity of Cyanogen Chloride

The purity of the cyanogen chloride was determined by the methods of Mauguin and Simon (4). The first of these involves hydrolysis of cyanogen chloride in an excess of standard sodium hydroxide and back-titration with standard sulphuric acid to a phenolphthalein end-point, care being taken not to make the solution acid:

$$\mathrm{CNCl} + 2\,\mathrm{NaOH} \quad \rightarrow \quad \mathrm{NaCNO} + \mathrm{NaCl}\ .$$

Alternatively, in the presence of a measured excess of sulphuric acid, hydrolysis of the cyanic acid occurs, and the sulphuric acid can be back-titrated with standard base in the presence of methyl red when hydrolysis is complete:

$$2\,\mathrm{HCNO} + \mathrm{H_2SO_4} \quad \rightarrow \quad \mathrm{(NH_4)_2\,SO_4} + \mathrm{CO_2}\ .$$

A third method was used, in which chloride was titrated with 0.03 N silver nitrate in the presence of dichlorofluorescein after hydrolysis of the cyanogen chloride.

Two methods were employed to get an accurately known weight of cyanogen chloride absorbed in sodium hydroxide. In Method A, a convenient quantity of cyanogen chloride at 0° C. was poured into 50 ml. of 0.5 N carbonate-free sodium hydroxide cooled to 0° C. The flask and contents were weighed at room temperature and atmospheric pressure before and after the addition of the cyanogen chloride. In Method B, the cyanogen chloride was sealed in a small vial with a long tip which could be broken off by pressure on a stopper after the vial had been placed in a flask containing sodium hydroxide. The weight of the vial was found by collecting and weighing the fragments.

Freezing Point Determinations

The method employed for freezing point determinations was an extension of that used by Morrison and Grummitt (5). The sample under investigation was contained in a small clear Dewar flask to which was sealed a stopcock at the top by means of which the air pressure between the walls could be adjusted to give a convenient rate of cooling when the Dewar flask was immersed in an ice–salt mixture at about −12° C. This vessel was fitted with a Beckmann thermometer and mechanically driven ring stirrer. The Beckmann thermometer was compared with two standard thermometers of different ranges. The zero points of these were checked with great care.

The vessel containing the sample of cyanogen chloride was placed in the ice–salt mixture, and time–temperature readings were taken until the freezing point had been passed. An ice–water bath was then substituted for the ice–salt mixture and readings were taken as before.

The cooling curve was of the conventional type for a pure compound. The freezing point could be determined accurately, but the melting point was not well defined.

In Table I, analytical and freezing point data are given for a series of samples of cyanogen chloride.

The molal freezing point lowering for cyanogen chloride was determined by measuring the freezing point depression produced when 0.7018 gm. of carbon

TABLE I

FREEZING POINT DATA AND PURITY OF CYANOGEN CHLORIDE BY CHEMICAL ANALYSIS

Freezing point, ° C.	Sample weight by method	Percentage purity		
		(1) By NaOH used	(2) By NH_3 produced	(3) By Cl present
−6.90	(1) 0.5645 *A*	100.9	—	—
	(2) 0.6375 *A*	100.5	—	—
	(3) 0.5517 *A*	101.0	—	—
−6.92	(1) 0.4742 *A*	101.8	—	—
	(2) 0.4529 *A*	100.7	—	—
	(3) 0.5062 *A*	100.2	—	—
−7.25	(1) 0.4342 *A*	98.8	—	—
	(2) 0.4722 *A*	99.2	—	—
	(3) 0.4527 *A*	99.3	—	—
−7.32	(1) 0.6647 *B*	100.3	—	—
	(2) 0.4770 *B*	96.5	—	—
	(3) 0.6970 *B*	96.2	—	—
−7.00	(1) 0.6218 *A*	99.67	—	99.8
	(2) 0.5476 *A*	99.90	—	100.8
−7.00	(1) 0.6006 *B*	99.85	99.9	99.4
	(2) 0.5758 *B*	99.10	98.9	99.4
	(3) 0.4878 *B*	99.55	99.5	99.2
−6.92	(1) 0.8762 *A*	99.88	—	100.5
	(2) 0.7169 *A*	100.32	—	100.2
−10.50	(1) 0.6039 *A*	89.3	—	—
	(2) 0.6445 *A*	88.6	—	—
	(3) 0.6134 *A*	88.1	—	—

tetrachloride was added to 24.186 gm. of cyanogen chloride. A lowering of 0.60° C. for a molality of 0.1886 was found, and the molal freezing point lowering is therefore 3.18° C. (calculated for CNCl, 3.19° C.). If the latent heat of fusion is assumed to be constant between −6.92° and −7.52° C., its value is 2720 cal. per mole. The entropy of fusion is 10 entropy units.

Vapour Pressure Measurements

The vapour pressure of cyanogen chloride was measured at various temperatures by a static method. A trap containing cyanogen chloride, and fitted with an Anschutz thermometer was connected to a mercury manometer. The trap was surrounded by a bath at the desired temperature contained in a Dewar flask. Readings were taken over such long periods of time that equilibrium was established between the cyanogen chloride and the bath, and the temperature of the cyanogen chloride was taken as that of the bath with only slight error. Observations were made over a period of nearly a week. The data, together with those of Klemenc and Wagner (3), are given in Table II.

The latent heat of vaporization calculated from the slope of the log p vs. $\frac{1}{T}$ line, using the Clausius–Clapeyron relation, is 6400 cal. per mole.

TABLE II

VAPOUR PRESSURE DATA FOR CYANOGEN CHLORIDE

Temperature, ° C.	Vapour pressure, mm. of Hg	
	Present values	Data of Klemenc and Wagner
−12	—	233
−10	—	265
− 8	—	302
− 6	342.1	341
− 5.6	348.3	—
− 4.8	359.1	—
− 4.0	—	373
− 2.8	396.3	—
− 2.0	—	408
0.00	446.8	445
0.00	446.5	—
1.85	483.6	—
2.00	—	484
3.40	515.4	—
4.00	—	527
5.00	558.0	—
6.00	—	573
6.20	581.2	—
7.40	616.5	—
8.00	—	621
9.10	658.3	—
10.00	—	674
10.60	697.3	—
12.00	—	730
12.80	754.8	—
13.00	763.0	—
14.00	—	790
17.82	916.5	—

The Hydrolysis of Cyanogen Chloride

Using material prepared as described previously, a brief study was made of the hydrolysis of cyanogen chloride in aqueous solutions buffered with carbon dioxide (pH 4 to 6). The steps in this reaction are (6, 7):

$$CNCl + H_2O \rightarrow HCNO + HCl$$

$$HCNO + H_2O \rightarrow NH_3 + CO_2$$

In solutions of pH less than 7, hydrolysis of cyanic acid is rapid at ordinary temperatures, and the first reaction is rate governing. A freshly prepared solution of pure cyanogen chloride was found to give no significant amount of precipitate with silver nitrate, hence the progress of reaction was followed by titration of chloride ion.

Portions of a freshly prepared solution of cyanogen chloride in distilled water saturated with carbon dioxide (pH between 4 and 6) were sealed into bulbs (all glass) and placed in thermostats controlled to ±0.05° C. The initial concentration of cyanogen chloride was determined by complete hydrolysis with excess 0.5 *N* sodium hydroxide solution and back-titration of the excess alkali to phenolphthalein end-point. The blank on the water saturated with carbon dioxide was also determined by adding excess standard alkali and back titrating. The extent of chloride ion formation after different periods of hydrolysis was determined by titration with 0.3 *N* silver nitrate, using dichlorofluorescein indicator.

Experiments were made without duplication for the following conditions:

Temperature, ° C.	Initial concentration, molarity	Extent of reaction studied, %
0.0	0.040	5
11.1	0.078	5
30.0	0.081	18
30.0	0.184	11
40.0	0.078	18
40.0	0.087	20
40.0	0.141	21
50.0	0.070	33
50.0	0.124	33

Data for 40° C., given in Table III, are typical of those obtained at other temperatures except 11.1° C., where for no obvious reason, somewhat greater variation about a straight line was noted when log $\frac{[CNCl]_{initial}}{[CNCl]_t}$ was plotted against time to yield the corresponding *k* values.

TABLE III

TYPICAL DATA FOR HYDROLYSIS OF CYANOGEN CHLORIDE AT 40° C.

Initial concentration, moles per litre

0.078		0.087		0.141	
Time, hr.	$[CNCl]_t$, moles/litre	Time, hr.	$[CNCl]_t$, moles/litre	Time, hr.	$[CNCl]_t$ moles/litre
4.6	0.075	3.4	0.084	3.4	0.136
6.8	0.073	9.6	0.079	9.6	0.128
17.5	0.065	13.1	0.076	13.1	0.123
—	—	18.0	0.072	18.0	0.117
—	—	23.5	0.069	23.5	0.110

The data indicate clearly that, over the limited range studied, the reaction was first order. The variation in first order rate constant with temperature may be summarized as follows:

Temperature, ° K.	k, hr.$^{-1}$
273.0	8.6×10^{-5}
284.1	3.1×10^{-4}
303.0	3.6×10^{-3}
313.0	1.2×10^{-2}
323.0	3.1×10^{-2}

A plot of log k vs. $\frac{1}{T}$ yielded an activation energy for the hydrolysis of approximately 21 kcal. per mole.

The addition of ammonium chloride to the extent of 0.01 M to two solutions of initial cyanogen chloride concentrations 0.052 M and 0.108 M gave no significant change in rate at 40° C. The addition of potassium nitrate in similar amount to a solution 0.056 M in cyanogen chloride resulted in approximately 25% increase in rate. Duplicate experiments were not made, but the effect of potassium nitrate is probably genuine.

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STUDIES ON THE FORMATION OF HEXAMINE[1]

MARY L. BOYD[2] AND C. A. WINKLER[3]

Abstract

Rate curves have been determined for the reaction of ammonia and formaldehyde in aqueous solution at 0° C. and 35° C., over a range of initial mole ratios (formaldehyde: ammonia) of 0.25 to 2.0. For each set of conditions, three curves have been obtained on the basis of ammonia consumed, formaldehyde consumed, and material precipitated with mercuric chloride respectively.

At 0° C. the three rate curves tend to approximate one another in a large excess of ammonia but are widely separated in excess formaldehyde. The reverse is true at 35° C. The reaction is characterized by a high initial rate of formation of hexamine, this rapid rate being maintained to a lower yield of hexamine the more dilute the solution. The existence of a stable by-product in excess formaldehyde is indicated by the variation in final yields of hexamine, when these are calculated on the basis of formaldehyde consumed, ammonia consumed, or material precipitated with mercuric chloride.

A mechanism for the reaction has been suggested.

Introduction

The only kinetic study of the reaction of formaldehyde with ammonia in aqueous solution to form hexamethylenetetramine (hexamine) was made by Baur and Rüetschi (1) in 1941. Their investigation showed that practically complete reaction took place and that the 'over-all' reaction could be represented by the equation:

$$6CH_2O + 4NH_3 = (CH_2)_6N_4 + 6H_2O.$$

The course of the reaction was followed by an acid titration of the ammonia. On the basis of rate constants calculated from the consumption of ammonia, Baur and Rüetschi (1) concluded that the reaction was third order with ammonia and formaldehyde in the molar ratio of 1:2.

A more complete study of the reaction between formaldehyde and ammonia in aqueous solution has been made, in which the rate of appearance of hexamine was followed simultaneously with the rate of disappearance of both formaldehyde and ammonia. These data should indicate whether there is any by-product formation and so present a more complete insight into the reaction of formaldehyde with ammonia in aqueous solution.

Experimental

Rate curves were determined at 0° C. and at 35° C. over a range of initial mole ratios (formaldehyde: ammonia) of 0.25 to 2.0. For each set of conditions, three curves were determined on the basis of ammonia consumed, formaldehyde consumed, and material precipitated with mercuric chloride.

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[1] *Manuscript received in original form February 20, 1947, and as revised, April 29, 1947. Contribution from the Department of Chemistry, McGill University, Montreal, Que.*

[2] *Graduate student, holder of two Studentships under the National Research Council of Canada. At present at the Bureau of Mines, Ottawa.*

[3] *Professor of Chemistry.*

The reaction was studied in 125 ml. stoppered Erlenmeyer flasks in an ice-bath (0° C.) and in a constant temperature water-bath maintained at 34.9° C. Ammonia solution (25 ml.) of the required strength was pipetted into the Erlenmeyer flasks, which were placed in the thermostat and allowed to come to the temperature of the bath. Formaldehyde solution (25 ml.) of the required strength, at the same temperature as the ammonia solution, was then added to each ammonia sample. Zero time was taken as the mid-point of the time required to drain the pipette. The reaction mixtures were shaken (to expedite removal of heat) for the desired times, after which the reaction was stopped with nitric acid (0.1 *N*). The end-point of the reaction was taken as the mid-point in the time required to make this acid titration. The sample was immediately placed in a 100 ml. volumetric flask and diluted to 100 ml. A 25 ml. aliquot was analysed for formaldehyde and a 50 ml. aliquot, for hexamine. The length of time between the end of the reaction (the acid titration) and the hexamine and formaldehyde analyses never exceeded three minutes. Preliminary experiments showed that there was no hexamine formed by the resulting ammonium nitrate and formaldehyde in the time required for these analyses.

Preparation of Reactants

Aqueous ammonia solutions were made by diluting reagent grade concentrated ammonia to the required strength and analysing the resulting solutions by acid titration with nitric acid (0.1 *N*).

Formaldehyde solutions were made by subliming paraformaldehyde into water. The resulting solutions were analysed by the potassium cyanide method.

Analytical Methods

The residual ammonia in the reaction mixture was determined by the acid titration, which also served to stop the reaction. Phenol red (pH range 6.8 to 8.4) was used as an indicator to avoid titration of the hexamine present. Preliminary experiments showed that hexamine was not titrated under these conditions.

The residual formaldehyde in the reaction mixture was determined by the potassium cyanide method. This is one of the standard methods of analysing for formaldehyde. The following technique was used. The 25 ml. aliquot of the diluted reaction mixture was introduced into an Erlenmeyer flask and to it a drop of phenolphthalein solution was added. It was necessary to add one or two drops of sodium hydroxide (0.1 *N*) to make the solution alkaline to phenolphthalein. Then a known volume of potassium cyanide (0.1 *N*) was added; usually 5 to 10 ml. in excess of that required to react with the formaldehyde present. The mixture was shaken and a known volume of silver nitrate (0.1 *N*) containing 20% nitric acid was added. The silver cyanide was filtered off and the filtrate titrated with potassium thiocyanate (0.1 *N*) using ferric alum as indicator. Preliminary experiments showed that the presence of hexamine does not affect the formaldehyde analysis.

The method of analysis for hexamine is based on the fact that hexamine and mercuric chloride form an insoluble complex (2, 3, 4). The method used is purely an empirical one and consists of precipitating hexamine under constant conditions. A calibration curve was established between known weights of hexamine in distilled water and the corresponding weights of the complex formed. Formaldehyde in amounts corresponding to its presence in the reaction mixture were without effect on the calibration curve, but the mercury–hexamine precipitate in the presence of excess ammonium ion was contaminated to the extent of about 2% by weight. A 50 ml. aliquot of the reaction solution, after titration with acid, was placed in an Erlenmeyer flask and 50 ml. water added, followed by 50 ml. mercuric chloride solution saturated at 40° C. After one-half hour, the precipitate was collected on a tared, sintered glass crucible, dried for one hour at 100° C., cooled, and weighed. The weight of hexamine was read from the calibration curves established under these reaction conditions.

Preliminary experiments showed that reaction–time data were reproducible to within approximately ±1.5% by the analytical methods used for ammonia and hexamine, and to within ±3% by formaldehyde analysis.

Results

Experiments were made at 0° C. to determine the effect of (i) changes in initial concentrations when the initial mole ratio is constant, and (ii) changes in the initial mole ratio with the initial concentration of formaldehyde or ammonia constant. The rate curves are plotted in Figs. 1, 2, and 3. The yield of hexamine is expressed as a percentage of the theoretical amount of hexamine for each particular set of initial concentrations. This theoretical yield is calculated on the basis of the initial concentration of that reactant which is not in excess. The three rate curves obtained for each experimental condition may be referred to, for convenience, as the ammonia curve, the formaldehyde curve, and the hexamine curve, when the yield is calculated on the ammonia consumed, the formaldehyde consumed, and the hexamine precipitated with mercuric chloride respectively.

The data reveal that under certain conditions there is a wide separation in the rate curves. Since all three curves are expressed in terms of hexamine, it is apparent that their separation demands interpretation of the analytical data.

The ammonia curve, which generally lies above the other two curves (but not in *A* and *B*, Fig. 2), would seem to correspond to a total of hexamine plus intermediates, the acid titration failing to titrate back the ammonia associated with the intermediates. Thus the consumption of ammonia, when expressed as hexamine, might logically correspond to curves of the type observed.

Where formaldehyde is in excess (Fig. 1) and also in two cases where ammonia is in excess (Curves *A* and *C*, Fig. 3), it is noted that the formaldehyde curve falls below the other two. This can be explained if, in the analysis for the residual formaldehyde in the reaction mixture, formaldehyde were analysed out of intermediates. If this analysis of formaldehyde out of intermediates but not out of hexamine itself be quantitative, the curve based on the consumption of formaldehyde should represent, to a good approximation, the actual rate of formation of hexamine. It follows from this argument,

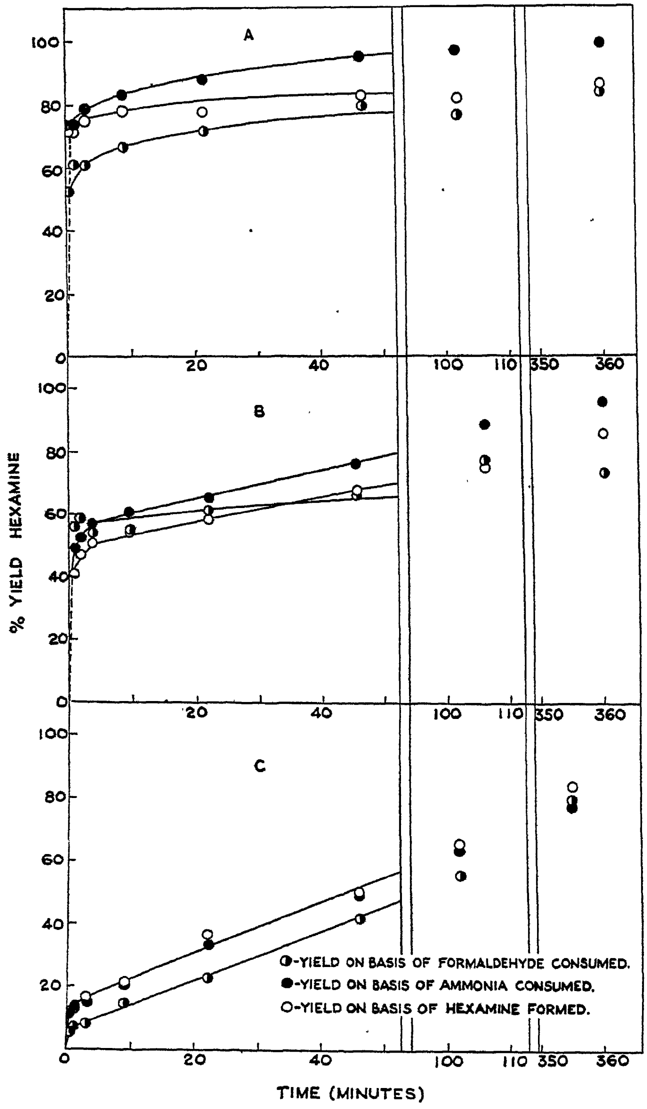


FIG. 1. *Rate curves for reaction at 0° C. Curves A—initial mole ratio (HCHO : NH_3), 1.88; initial concentrations—0.195 mole per litre ammonia, 0.367 mole per litre formaldehyde. Curves B—initial mole ratio (HCHO : NH_3), 1.85; initial concentrations—0.0964 mole per litre ammonia, 0.179 mole per litre formaldehyde. Curves C—initial mole ratio (HCHO : NH_3), 1.96; initial concentrations—0.0502 mole per litre ammonia, 0.0984 mole per litre formaldehyde.*

that when the hexamine curve lies above the formaldehyde curve, the mercuric chloride must precipitate something other than hexamine. Since the three curves generally do not converge at the end-point, it may be assumed that a stable by-product is formed.

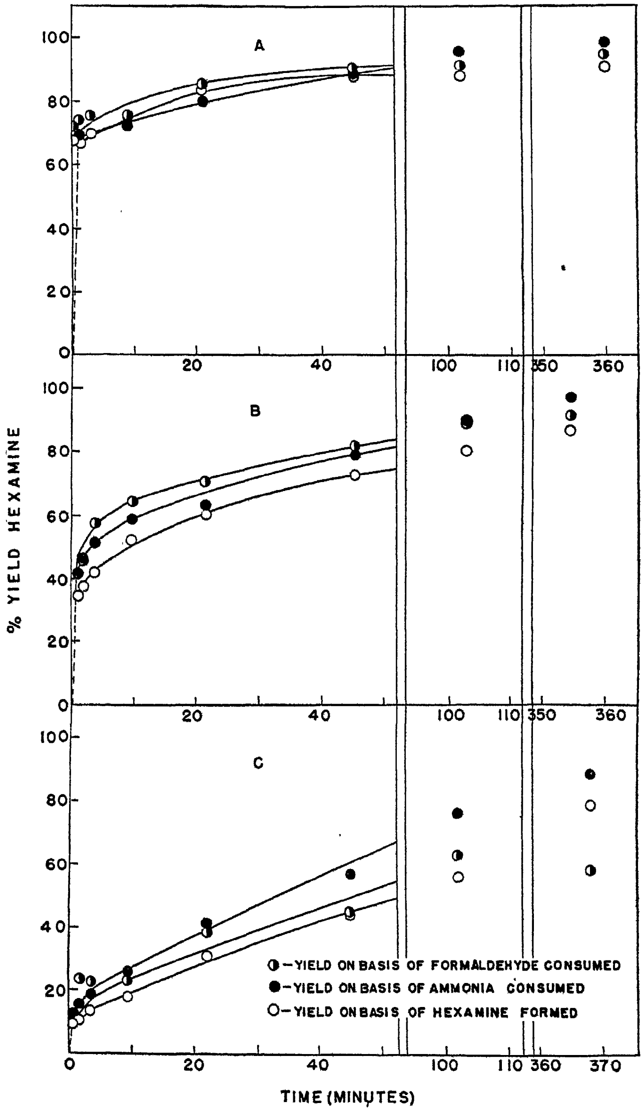


FIG. 2. *Rate curves for reaction at 0° C. Curves A—initial mole ratio (HCHO : NH_3), 0.25; initial concentrations—0.754 mole per litre ammonia, 0.190 mole per litre formaldehyde. Curves B—initial mole ratio (HCHO : NH_3), 0.24; initial concentrations—0.398 mole per litre ammonia, 0.0968 mole per litre formaldehyde. Curves C—initial mole ratio (HCHO : NH_3), 0.24; initial concentrations—0.194 mole per litre ammonia, 0.0475 mole per litre formaldehyde.*

The relative positions of the formaldehyde curves indicate that, in the early stages of the reaction, the amount of formaldehyde consumed increases as the initial mole ratio (formaldehyde : ammonia) decreases. (Curves *B*, Fig. 1

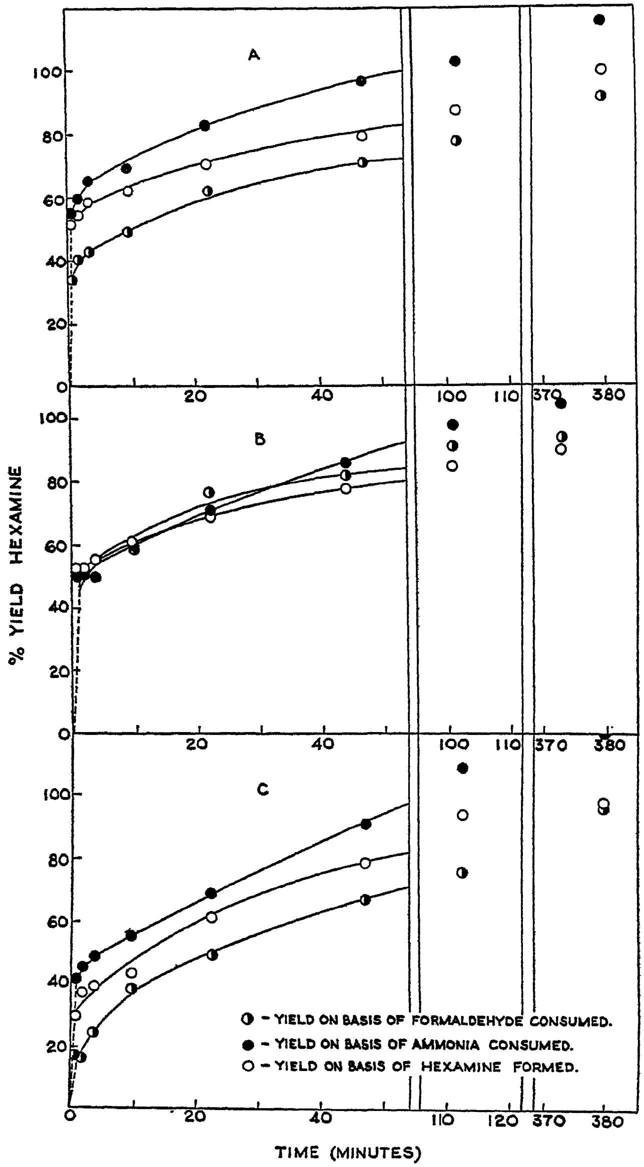


FIG. 3. *Rate curves for reaction at 0° C. Curves A—initial mole ratio (HCHO : NH_3), 0.94; initial concentrations—0.195 mole per litre ammonia, 0.183 mole per litre formaldehyde. Curves B—initial mole ratio (HCHO : NH_3), 0.64; initial concentrations—0.280 mole per litre ammonia, 0.179 mole per litre formaldehyde. Curves C—initial mole ratio (HCHO : NH_3), 0.46; initial concentrations—0.195 mole per litre ammonia, 0.0895 mole per litre formaldehyde.*

and Curves *C*, Fig. 3 are exceptions). Following the argument outlined above, this means that as the formaldehyde curve moves upward, less and less formaldehyde is being analysed out of the intermediates, and this, in turn, indicates that the reaction may take place along at least two different paths. Along the path which is preferred when formaldehyde is in excess, formaldehyde is analysed out of the intermediates, whereas along the path preferred when ammonia is in excess, the amount of formaldehyde analysed back from the intermediates is less.

In the series of experiments where the initial mole ratio was kept constant at 2.0 and in a second series where the initial mole ratio was constant at 0.25, it is noted that the high initial rate of formation of hexamine is maintained to a lower yield of hexamine the more dilute the solution. (Figs. 1 and 2).

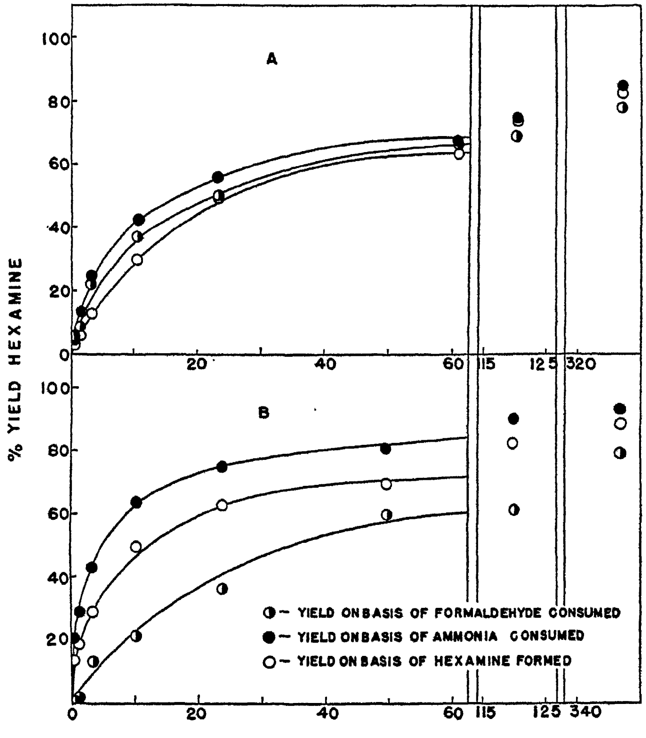


FIG. 4. *Rate curves for reaction at 34.9° C. Curves A—initial mole ratio (HCHO : NH_3), 2.03; initial concentrations—0.0507 mole per litre ammonia, 0.103 mole per litre formaldehyde. Curves B—initial mole ratio (HCHO : NH_3), 0.25; initial concentrations—0.208 mole per litre ammonia, 0.0520 mole per litre formaldehyde.*

To investigate the effect of raising the temperature of the reaction, experiments were repeated at 34.9° C. The rate curves for these experiments are plotted in Fig. 4. The shape of the rate curves is quite different from that at 0° C. The rate in the early stages of the reaction is slower than at 0° C.

This would suggest that one route whereby hexamine was formed at 0° C. has been largely eliminated at 35° C. The effect of changing the initial mole ratio (formaldehyde : ammonia) at 35° C. is opposite to the effect produced by varying it at 0° C. For an initial mole ratio of 2.0, considerable formaldehyde is analysed out of the intermediates at 0° C. whereas a small amount is analysed out at 35° C., at comparable initial concentrations of formaldehyde and ammonia. Similarly, for an initial mole ratio of 0.25, a relatively small amount of formaldehyde is analysed back at 0° C. while at 35° C. a large amount is analysed out of the intermediates. The fact that two different types of curves were obtained at 35° C. would indicate that if two different paths exist, they have different activation energies.

A large number of samples of hexamine – mercuric chloride complex precipitated in the preceding experiments were analysed for formaldehyde and ammonia. The results showed that the complex is not contaminated with formaldehyde but is contaminated with ammonia to the extent of 2%.

Order of the Reaction

Baur and Rüetschi (1) considered the reaction between formaldehyde and ammonia in aqueous solution to be third order, the rate being proportional to $[NH_3] \times [HCHO]^2$.

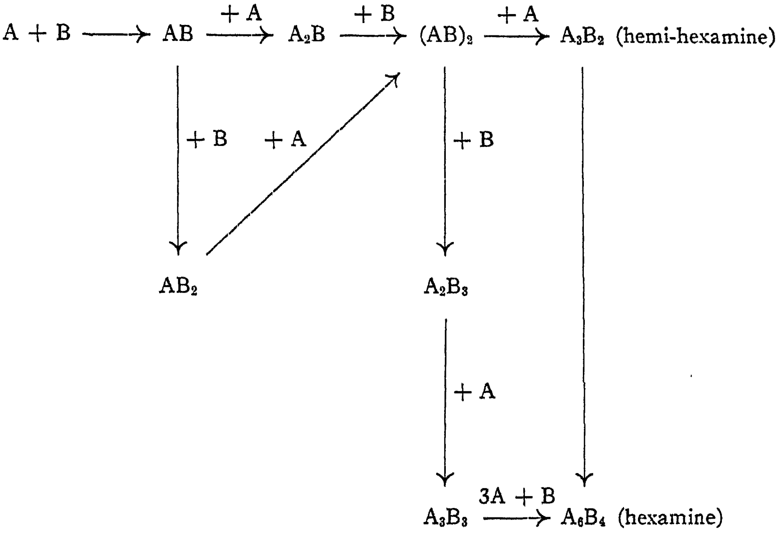
The analytical data of the present study indicate that the reaction is complex. A determination of the order of the competing reactions would require many more kinetic data than are at present available.

Mechanism of the Reaction

The results of the present investigation indicate that any mechanism proposed for the reaction must account for several characteristics of the reaction. These are as follows:— (1) There is a high initial rate of formation of hexamine, this rapid rate being maintained to a lower yield of hexamine the more dilute the solution. This high initial rate is followed by a rapid transition to a much slower rate. (2) At 0° C., the rates of reaction inferred from the rates of disappearance of the two reactants and from the rate of formation of hexamine show discrepancies which indicate that at least two paths may lead to formation of hexamine, one path being preferred when ammonia is in excess, the other preferred when formaldehyde is in excess, and that more formaldehyde may be analysed back from intermediate bodies under these latter conditions. (3) Final yields of hexamine differ, depending upon whether they are calculated on the basis of ammonia consumed, formaldehyde consumed, or material precipitated with mercuric chloride. The implication is that a stable by-product may be formed under suitable conditions. (4) When the temperature was increased to 35° C. the consumption of formaldehyde, in the presence of excess formaldehyde, was greater relative to the consumption of ammonia than at 0° C., while in excess ammonia the reverse was true. Moreover, the effect of increased temperature was to reduce the rate of hexamine formation in the early stages of the reaction.

A two path type of mechanism may be illustrated by the following:—

(A = HCHO) (B = NH_3)



This scheme is meant primarily to indicate possible alternative paths, and does not include all the reactions theoretically possible, nor is it particularly concerned with the steps leading to hexamine formation from the cyclic triamine and from hemi-hexamine. Disregarding the identity of the intermediate compounds postulated above, and assuming that the alternate paths lead from the dimer $(AB)_2$, the path to hemi-hexamine should be favoured in excess formaldehyde while that leading to A_3B_3 should be favoured in excess ammonia.

Additional postulates to account for the observed behaviour are: (1) rapid equilibrium between monomer and dimer; (2) formaldehyde but not ammonia analysed from the dimer and monomer; and (3) an activation energy for the formation of the monomer that is less than that for reaction of the dimer with formaldehyde but greater than that for reaction of the dimer with ammonia.

The observed separations of the three rate curves are readily accounted for by this mechanism. If formaldehyde is analysed from $(AB)_2$ while ammonia is not, it is obvious that the formaldehyde and ammonia curves cannot coincide. Also, the scheme would serve to explain, as the experiments indicate in a general way, that in the early stages of reaction less formaldehyde is analysed out of intermediates as the initial mole ratio of formaldehyde:ammonia is decreased. In excess ammonia, reaction of $(AB)_2$ with B should predominate over its reaction with A. Therefore, $(AB)_2$ should be removed rapidly from the system and its concentration be small. Hence little formaldehyde should be analysed from this intermediate. In excess formaldehyde reaction of $(AB)_2$ with A should be favoured but if the activation energy along this path be somewhat greater than along the alternative path, the rate of removal of

$(AB)_2$ should be smaller, more $(AB)_2$ should be present in the system and, therefore, more formaldehyde should be analysed from it. The reversal of this behaviour at 35° C. can be explained when the relative activation energies assigned to the formation of monomer, reaction of the dimer with formaldehyde, and reaction of the dimer with ammonia, are taken into consideration.

The question arises as to the identity of the various compounds involved as intermediates. If formaldehyde be regarded as $CH_2(OH)_2$ in aqueous solution, then a unified picture of the reaction mechanism previously given can be drawn, following the principle that formaldehyde reacts to form methylol compounds and ammonia reacts at methylol groups. According to this scheme, the dimer $(AB)_2$ may be represented as a methylol amine, $HO . CH_2 . NH . CH_2NH_2$. This type of compound seems more probable than the one step trimerization of AB postulated by Baur and Rüetschi (1). Similarly, A_2B_3 may be represented by $H_2N . CH_2 . NH . CH_2 . NH_2$. Although hypothetical, it is analogous to methylene diamine, derivatives of which are known (5). A_3B_3 becomes the cyclo-trimethylenetriamine which has already been postulated many times (1). Hemi-hexamine is also assumed to be formed as a linear dimethylol compound which, by condensation of two molecules with loss of four molecules of water forms hexamine.

There is little point in speculating on the structure or origin of the by-product since no evidence as to its nature was obtained here. It is interesting, perhaps, that it could be a cyclic oxide formed by one mode of water elimination from the linear dimer of hemi-hexamine.

If subsequent investigation demanded it, alternative paths might be assumed to originate at the monomer AB. The type of arguments applicable would remain essentially unaltered, but the postulates would then be framed in terms of the monomer rather than the dimer.

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A RECORDING UNIT AND ELECTRONIC SHUNT SELECTOR FOR A MASS SPECTROMETER[1]

BY F. P. LOSSING,[2] R. B. SHIELDS,[3] AND H. G. THODE[4]

Abstract

A direct action shunt selector has been designed that pre-selects the appropriate shunt so that widely different mass spectrometer ion currents can be recorded linearly on a standard chart. In conjunction with a linear direct current amplifier and a Leeds and Northrup Speedomax pen recorder, this unit allows rapid and accurate recording of a given mass spectrum, which can be scanned by varying either the magnetic field or the ion accelerating potential of the mass spectrometer. When used with a 180° Nier type mass spectrometer with well stabilized circuits, a precision of ±0.2% in measuring the ratio of CO_2^{45} and CO_2^{46} was obtained. Also, samples of xenon were investigated and the abundances of the isotopes determined.

Introduction

The usefulness of the mass spectrometer is greatly extended by the utilization of some means of fast automatic recording of the ion currents. In hydrocarbon analysis automatic recording is a practical necessity owing to the presence of many ion peaks spread over a considerable mass range. A recording system must be capable of allowing accurate measurement of ion currents varying by a factor of 1000; and, for such to be the case, it is obvious that some means must be provided for varying the sensitivity of the recording instrument so that small peaks will give a deflection of the same order of magnitude as large peaks.

Various methods of accomplishing this have been devised. Smith, Lozier, Smith, and Bleakney (3) used a galvanometer light-beam and a wide chart of photographic paper. Washburn, Wiley, and Rock (4) used four galvanometers recording simultaneously at four sensitivity levels on photographic paper. This method has been incorporated into the Consolidated Engineering Corporation mass spectrometer. Hipple, Grove, and Hickam (1) described a method using pen recording built around a Leeds and Northrup Speedomax recorder. Extension of the scale was obtained by reducing the sensitivity of the recorder as the deflection increased, thereby giving an essentially logarithmic scale. To record peak heights too large for this scale, a limit switch at the upper end of the chart changed the sensitivity level by means of a shunt. Later, J. A. Hipple developed a means for recording on a linear scale. Each peak was first traced on a logarithmic scale, and then re-traced on a linear scale, the shunt being determined by the height of the logarithmic peak.

Inghram (2) used a Brown Electronik Strip Chart Recorder whose sensitivity could be set at at least two levels. No mention is made of the method of changing sensitivity.

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[1] *Manuscript received April 25, 1947.*
Contribution from the Department of Chemistry, McMaster University, Hamilton, Ont.

[2] *Chemist, Division of Chemistry, National Research Council of Canada, Ottawa, Canada.*

[3] *Physicist, Division of Atomic Energy, National Research Council of Canada.*

[4] *Professor.*

The system described in this paper is similar to that used by Hipple *et al.*, in that a Speedomax pen recorder is used, but the logarithmic scale is replaced by a linear scale, and the resulting increase in deflection is handled by having a number of shunts of different sensitivities. An electronic shunt selector was designed and built which, operated by the d-c. amplifier output voltage, selects the appropriate shunt while the Speedomax pen is travelling up the forward side of the peak.

Experimental

A block diagram of the system is given in Fig. 1. The electrometer tube is a 954 acorn tube used as a space-charge tetrode feeding a stabilized, direct current, feedback amplifier. The negative output voltage is filtered to remove a-c. components and applied across the system of shunts. The sensitivity level of recording depends on the proportion of this signal that is applied to the Speedomax, and is controlled by the relays, which connect the negative lead from the Speedomax to one of the six positions along the shunt system. The amplifier output voltage is also applied to the selector circuit which determines which relay should be closed to give the sensitivity level appropriate to that voltage.

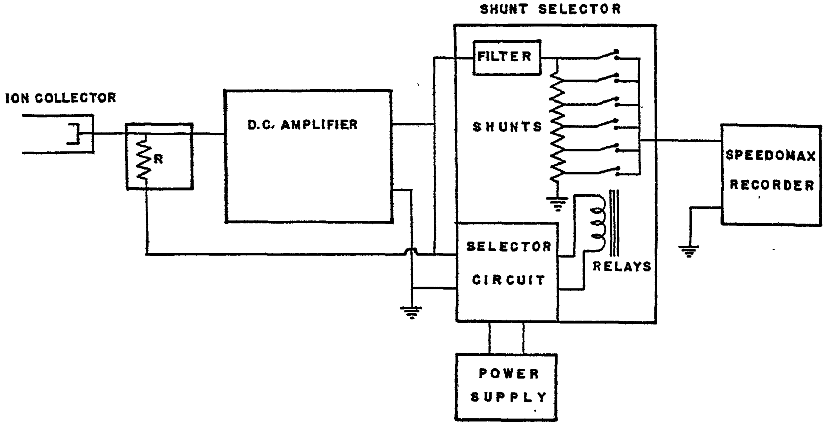

FIG. 1. *Block diagram of recording system.*

A schematic diagram of the shunt selector circuit is given in Fig. 2. The power supply shown for this unit delivers 250 v. at 200 ma. with a ripple of less than 0.004 v. R.M.S. The output voltage can be made almost independent of line voltage fluctuations by proper adjustment of R_2. The heaters of all the critical tubes are connected in series and operated from this stabilized supply in order to reduce the drift.

The negative signal output voltage from the d-c. amplifier is applied to the grid of the cathode follower tube T_{10}, which isolates the d-c. amplifier from the grid current drawn by T_{11}, T_{14}, T_{17}, etc. The potentiometer R_{16} is set to give zero volts output with zero volts input. The output voltage from the cathode follower is amplified by the circuits associated with T_{11},

T_{12}, T_{14}, T_{15}, T_{17}, T_{19}, and T_{21}, and applied as a positive signal to the control grids of the thyratrons T_{13}, T_{16}, T_{18}, T_{20}, T_{22}. By means of the potentiometer R_{20}, the thyratron T_{13} can be set to fire at a voltage corresponding to full scale deflection on the Speedomax which is connected (at no signal) to the position of maximum sensitivity by the relay S_3. When a signal larger than this voltage is applied, thyratron T_{13} fires, closing relay S_4 and breaking the current to relay S_3. The Speedomax is thus disconnected from its previous position and connected to the point between R_{68} and R_{69}, where its sensitivity is reduced to one-third of the previous value. In practice,

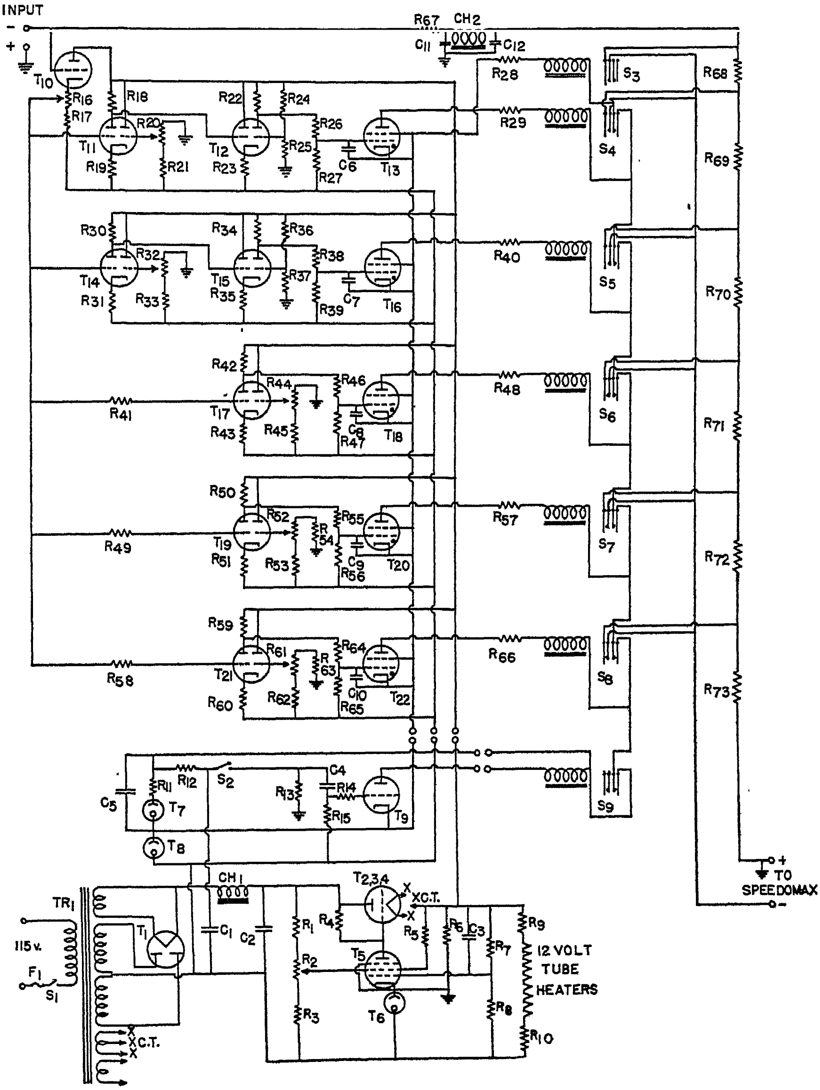

FIG. 2. *Circuit of shunt selector.*

the setting of the firing voltage is made by applying a signal giving full scale deflection and advancing the helipot R_{20} until the thyratron T_{13} just fires. The other thyratrons are adjusted similarly by means of R_{32}, R_{44}, R_{52}, R_{61} to fire at full scale deflection on the other shunts.

As a large peak is scanned, the pen travels up the chart until the signal is sufficient to fire the first thyratron. At the reduced sensitivity the pen takes up a lower position, causing a step to be traced, and continues to rise with increasing signal voltage. This process is repeated until a sensitivity level is reached that allows the top of the peak to be traced. The number of this shunt can be determined by the number of steps produced in this way on the forward side of the peak (see Fig. 4). Each peak height must be multiplied by the corresponding shunt factor to give the peak height relative to the most sensitive shunt. The zero signal level for each shunt must be determined by setting the pen just above zero on the most sensitive shunt and closing the relay contacts for each shunt in turn. These zero signal levels were found to vary owing to small changes in the amount of magnetic pickup in the shunt system. Better shielding of the shunt system should eliminate this variation.

When the pen returns to the zero signal line after a peak has been traced, it closes a limit switch S_2 applying a positive pulse to the grid of tube T_9 long enough to close relay S_9, which extinguishes the thyratrons and returns the Speedomax connection to the position of maximum sensitivity at relay S_8. With the shunt values shown, the sensitivities on the different shunts are in the ratio 1, 1/3, 1/10, 1/30, 1/100, and 1/300, and no peak will have a height of less than 1/3 of the full width of the chart.

The position of the pen on the chart always lags behind the signal voltage by a distance depending on the slope of the side of the peak; the pen never reaches the top of the chart, since the shunt selector responds instantaneously to the signal voltage. For this reason the pen is always closer to the deflection it should have on the next shunt than it would be if the shunts were selected by means of a limit switch at the top of the chart. In spite of this, it is found occasionally, with sharp-topped peaks, that the top of a peak is traversed just after a change of shunt has occurred. In these cases the pen drops to a value on the 'trailing edge' of the peak, missing the top entirely. One solution for this contingency is that of re-scanning at a slightly increased or decreased ion current, or changing the firing voltage for that shunt. Another solution has been provided by Hipple *et al.* (1). It should be emphasized, however, that this situation arises less often with the shunt selector than with a limit switch owing to the reason given above. With mass spectrometer tubes giving square topped peaks, this difficulty is not encountered; the pen drops to the flat portion of the top.

The mass spectrometers used in this work were Nier type 180° and 90° instruments with well stabilized circuits. Scanning of the mass spectrum can be obtained by varying either the ion accelerating voltage or the deflecting field current of the mass spectrometer. Both methods were used. Smooth variation of either the potential or the current was obtained by means of a helipot in the control circuit of the regulated supply concerned. The helipot was driven by a variable speed motor with a reversing switch so that scanning in both directions was possible. This was useful for obtaining average values when very small samples of gas were being investigated, since the ion currents may decrease with time.

Some mass spectrometer tubes may show mass discrimination when magnetic scanning is employed, while others may show mass discrimination when electrostatic scanning is employed. The availability of both methods is very useful, since, when both methods give the same results, it is likely that mass discrimination effects are at a minimum. These effects are important for isotope abundance measurements, but are not important in hydrocarbon analysis where a calibration of the instrument is made.

Results

Fig. 3 shows a typical set of xenon isotope peaks obtained at one sensitivity level, that of the most sensitive shunt. In this case the gas pressure was lowered until the highest peak (132) gave almost full scale deflection. At this low pressure, the 124 and 126 isotopes do not even register. In Fig. 4 the pressure has been increased until the 124 and 126 isotopes give an appreciable deflection, and the isotopes of greater abundance are traced on shunts of lower sensitivities because of the action of the shunt selector. In both figures the zero signal line appearing is that of the most sensitive shunt, so that the apparent rise in this line in Fig. 4 due to background between the peaks is negligible compared to the great height of these peaks when multiplied by the corresponding shunt factor.

In each case the direction of scanning was from high mass to low mass. On the leading or high mass side of each large peak may be seen the series of zigzags due to the successive selection of shunts of decreasing sensitivities, and on the low mass side of the peaks may be seen another zigzag caused by the action of the switch which returns the recorder to full sensitivity when the pen returns to the zero signal line.

The abundance of the isotopes of xenon were measured from automatically recorded spectrograms similar to Fig. 4 and are given in Table I. A more precise determination of isotopes 124 and 126 could be obtained at higher ion currents.

A sample of carbon dioxide was also investigated, and mass 45/46 ratios measured from the chart are given in Table II. For the set of 15, the per cent average deviation from the mean is ±0.21%, and the probable error of the mean is 0.0014 or 0.05%. These results were obtained with a 180° type mass spectrometer that gave sharp-topped peaks, because of the geometry of the tube. With a 90° type mass spectrometer giving square-topped peaks, because of wider exit slits, mass 44/46 ratios were obtained with a per cent average deviation from the mean of ±0.1%.

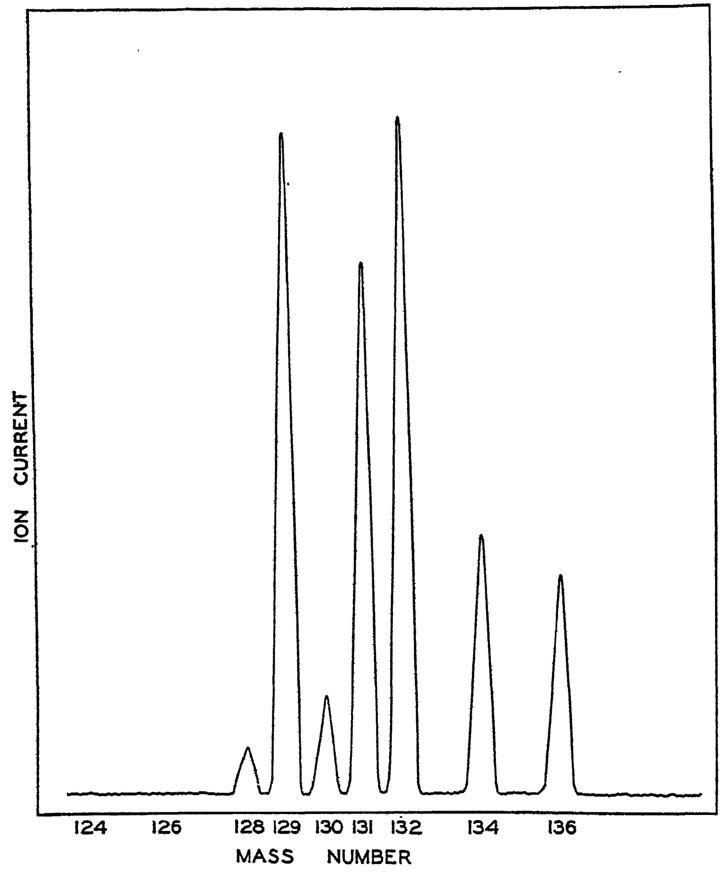

FIG. 3. *Xenon isotopes recorded at one sensitivity level.*

TABLE I

PERCENTAGE CONSTITUTION OF XENON

	Mass abundance								
	124	126	128	129	130	131	132	134	136
Trial 1	0.095	0.089	1.925	26.30	4.050	21.20	26.90	10.55	8.98
Trial 2	0.096	0.088	1.915	26.12	4.060	21.28	26.95	10.51	8.91
Trial 3	0.094	0.086	1.910	26.30	4.050	21.25	26.95	10.50	8.90
Average Deviation	0.095 ±0.001	0.088 ±0.001	1.917 ±0.006	26.24 ±0.08	4.053 ±0.004	21.24 ±0.03	26.93 ±0.02	10.52 ±0.02	8.93 ±0.03

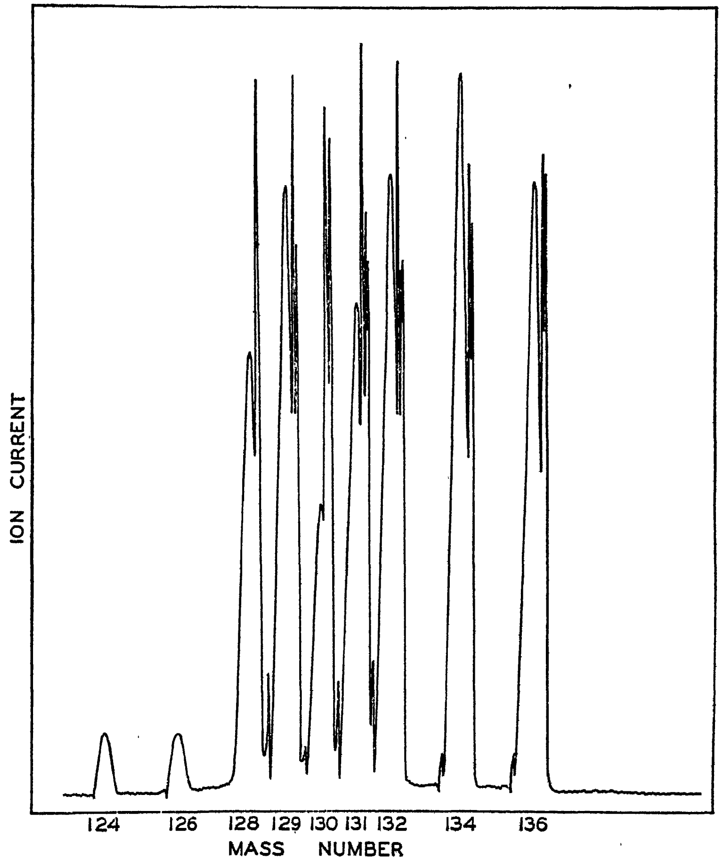

FIG. 4. *Xenon isotopes recorded using shunt selector.*

TABLE II

RATIO OF CO_2^{45} TO CO_2^{46}

Peak height, cm.		Ratio 45/46	Deviation
45	46		
57.15	19.52	2.928	0.003
57.24	19.58	2.924	0.001
57.06	19.52	2.923	0.002
57.18	19.50	2.931	0.008
56.94	19.48	2.923	0.002
56.64	19.42	2.917	0.008
56.70	19.50	2.910	0.015
57.00	19.50	2.923	0.002
56.94	19.32	2.947	0.022
56.76	19.32	2.938	0.013
56.64	19.40	2.920	0.005
56.40	19.30	2.922	0.003
56.55	19.32	2.927	0.002
56.55	19.32	2.927	0.002
56.40	19.32	2.919	0.006
		Average 2.925	±0.0062

Discussion

In addition to the obvious advantages of automatic recording for hydrocarbon analysis with the mass spectrometer, its application to the measurement of isotope abundance results in a higher degree of precision than that obtainable by measurement of galvanometer deflection. To obtain the abundances of the xenon isotopes by the manual method takes considerable time, during which changes in the gas pressure, filament characteristics, and electronic circuit characteristics might occur. With automatic recording the nine isotopes of xenon are scanned in two minutes or less, during which time the amount of change in these factors is very much smaller. The ratio of any two isotopes can be rapidly and accurately measured by scanning them alternately until 10 or 20 ratios have been obtained.

The question arises as to the usefulness of recording equipment for routine isotope abundance measurements where only two isotopes are involved, as for example C^{13}, N^{15}, and O^{18} assay work. If 1% accuracy is sufficient it is debatable whether automatic recording equipment is justified. However, where high precision is required as in the determination of small differences in isotopic content of two samples, the recording equipment has been found most useful. This work involves the determination of exchange factors for isotopic reactions and small differences in the isotopic constitution of the light elements, depending on the source. The precision obtainable for routine O^{18} determinations has been extended to 0.1% of its normal concentration.

Acknowledgments

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THE KINETICS OF THE FORMATION OF ETHANOLAMINES[1]

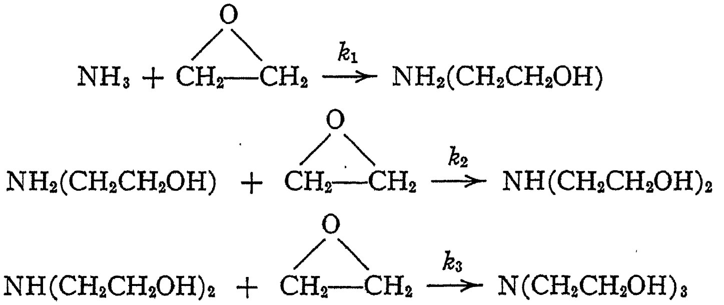
By C. Potter[2] and R. R. McLaughlin[3]

Abstract

The formation of ethanolamines from ethylene oxide and ammonia is a case of simultaneous, consecutive, competitive second order reactions. The results obtained show the time at which to stop a reaction for a maximum yield of any one of the three products. It is shown that as the reaction proceeds from ammonia to monoethanolamine to diethanolamine to triethanolamine the velocity constants are in the ratio of 1 : 6 : 4 for the three reactions. The values of the velocity constants are determined graphically. From these values an energy of activation of 16,600 cal. is calculated and is the same for each step. There is an indication that a tetraethanol - ammonium hydroxide is slowly formed.

Introduction

This research on the kinetics of formation of ethanolamines was undertaken to find the data necessary for the calculation of the maximum production of diethanolamine by a continuous process. The reactions taking place when ethylene oxide reacts with ammonia are (5, 6, 7, 8, 9, 15):



$$NH_3 + \overset{O}{CH_2\text{—}CH_2} \xrightarrow{k_1} NH_2(CH_2CH_2OH)$$

$$NH_2(CH_2CH_2OH) + \overset{O}{CH_2\text{—}CH_2} \xrightarrow{k_2} NH(CH_2CH_2OH)_2$$

$$NH(CH_2CH_2OH)_2 + \overset{O}{CH_2\text{—}CH_2} \xrightarrow{k_3} N(CH_2CH_2OH)_3$$

Other methods involve the use of ethylene chlorohydrin (17) in place of ethylene oxide, ammonium salts (10, 12), and recently a gas phase reaction has been patented.

The mathematical treatment covering the theory of consecutive competitive reactions as exemplified by the experimental work presented here, has been presented (11) and the following equations developed:

$$y_1 = \frac{y_0}{1-\alpha}\left(y_0^{\alpha-1} - 1\right)$$

$$y_2 = \alpha y_0\left[\frac{y_0^{\beta-1}}{(\alpha-\beta)(1-\beta)} - \frac{y_0^{\alpha-1}}{(\alpha-\beta)(1-\alpha)} - \frac{1}{(\alpha-1)(\beta-1)}\right]$$

$$3 - Y = Ay_0^{\alpha} + By_0^{\beta} + Cy_0$$

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Contribution from the Department of Chemical Engineering, University of Toronto, Toronto, Ont. Condensed from a portion of a thesis submitted in partial fulfilment of requirements for the degree of Ph.D.

[2] *Graduate student.*

[3] *Professor.*

$$A = \frac{1}{1-\alpha} - \frac{\beta}{(\alpha-\beta)(1-\alpha)} \qquad B = \frac{\alpha}{(1-\beta)(\alpha-\beta)}$$

$$C = 1 - \frac{\alpha}{1-\alpha} + \frac{\alpha\beta}{(1-\alpha)(1-\beta)}$$

$$Y = y_1 + 2Y_2 + 3Y_3$$

$$= 3 - 3y_0 - 2y_1 - y_2$$

$$y_3 = 1 - y_0 - y_1 - y_2$$

$$\frac{k_2}{k_1} = \alpha; \quad \frac{k_3}{k_1} = \beta$$

y_0 = moles of ammonia present per mole original ammonia

y_1, y_2, y_3 = moles of amine per mole original ammonia

Y = moles ethylene oxide used up per mole ammonia

k_1, k_2, k_3 = velocity constants.

Experimental Procedure

Epitome

The rate at which ethylene oxide reacts with ammonia was determined as follows. A weighed amount of ethylene oxide in a small test-tube was dropped into a larger one containing a definite quantity of ammonium hydroxide. The larger tube was tightly stoppered and placed in a constant temperature bath for a definite period. At the end of the desired time, the tube containing the reaction mixture was opened and rinsed into a volumetric flask containing hydrochloric acid for stopping the reaction, and the resulting solution was analysed for ammonia and ethanolamines.

(*a*) *The Reaction*

Standardized ammonium hydroxide solution was measured into the larger test-tube. Ethylene oxide from a cylinder was passed through a soda-lime tower, through a downward spiral ice condenser, and collected in slight excess of the desired amount in a small weighed test-tube placed upright in a beaker (or other suitable container). The test-tube and beaker were placed on the balance with the desired weight on the other pan and evaporation of the excess ethylene oxide allowed to take place. When the correct weight had been reached the test-tube was quickly removed and dropped into the ammonium hydroxide solution, the time observed, the larger tube sealed and the stopper wired down. Finally, the tube was placed in a constant temperature bath. It was shaken at frequent intervals to ensure complete mixing.

When known amounts of ethylene oxide and ammonia were mixed and the reaction allowed to go to completion, the experiment was called a static run. When the reaction had been stopped before it had reached completion and the time of reaction measured, the experiment was called a kinetic run.

Kinetic runs were made at 10°, 20°, and 30° C. Static runs were made at room temperature and the samples allowed to stand for four days before being analysed.

The kinetic run at 10° C. was started with 6.2 gm. ethylene oxide, 10 ml. 3.493 *N* ammonium hydroxide and 10 ml. water. The kinetic runs at 20° and 30° C. were started with the same amounts of reagents but with 25 ml. water instead of 10 ml. in order to retard by dilution the reaction rate. In the static runs varying quantities of ethylene oxide were mixed with a fixed quantity of ammonium hydroxide, viz.: 10 ml. 3.613 *N* ammonium hydroxide and 25 ml. water. After reaction had taken place for the desired time in the kinetic runs, the samples were rinsed into a 250 ml. volumetric flask, containing 25 ml. 12 *N* hydrochloric acid used to stop the reaction (twice the total number of moles of original ammonia and ethylene oxide present) and made up to volume. In the static runs, hydrochloric acid to stop the reaction was unnecessary, since the reaction would be virtually complete because it had been allowed to take place for four days.

It will be noted from this description that the points on any one of the curves of Fig. 1 are based upon separate reaction mixtures for each point.

(*b*) *Analytical Procedure*

(i) *Aeration.*—The mixture of ammonia and amines was analysed by aerating (16) the sample to remove the ammonia and separating the amines by the Hinsberg method, using *p*-bromobenzenesulphonyl chloride. Air, washed by passing through 10% sulphuric acid, was passed through the sample and then through a 5% boric acid solution to absorb the ammonia evolved.

(ii) *Ammonia separation.*—A test-tube charged with a 25 ml. sample of reaction mixture was connected to a second test-tube containing 50 ml. of 5% boric acid solution. Saturated potassium carbonate solution (10 ml.) was added to the sample. Air was drawn very slowly through the apparatus for five minutes by means of suction and then rapidly for 30 min. Finally the sample tube was immersed to a depth of 2 in. in a 400 ml. beaker of water (100° C.) and aspiration continued for another 30 min., without further heating of the water-bath.

The ammonia absorbed in the boric acid was determined by titration with standard sulphuric acid, using a mixed bromocresol green and methyl red indicator.

(iii) *Amine separation.*—The contents of the sample tube were neutralized to a methyl orange end-point with concentrated hydrochloric acid, and 2 gm. sodium bicarbonate, 25 ml. of acetone, and 2 gm. of *p*-bromobenzenesulphonyl chloride added. The tube was placed in a hot water-bath and the acetone slowly evaporated, with occasional stirring. The solution was then cooled, and 10 ml. 10% wt./vol. sodium hydroxide, 20 ml. alcohol, and a small piece of porous tile added. The tube was then returned to the water-bath for evaporation of the alcohol.

From this point the separation of mono- and diethanolamine was made with chloroform as described by Shupe (14). The stopcocks on the separating funnels were greased with colloidal graphite.

(iv) *Correction of analytical figures.*—Having developed the method just described as the most suitable available for the reaction mixtures involved, we analysed a series of samples from a kinetic run by this method. Artificial mixtures of ammonia, monoethanolamine, diethanolamine, and triethanolamine corresponding with the results obtained were made up and analysed in the same way. The differences between the known and analytical values appear in Table I, and were used as corrections in all reported results. The values for ammonia required no correction.

TABLE I

ANALYTICAL CORRECTIONS

Moles ammonia	Moles monoethanolamine per mole ammonia			Moles diethanolamine per mole ammonia		
	Present	Found	Correction	Present	Found	Correction
0.90	0.0690	0.0689	+0.0001	0.0210	0.0211	−0.0001
0.70	0.1120	0.1091	+0.0029	0.0960	0.0793	+0.0167
0.50	0.0970	0.0952	+0.0018	0.1390	0.1314	+0.0076
0.30	0.0650	0.0700	−0.0050	0.1080	0.1040	−0.0040
0.10	0.0310	0.0431	−0.0121	0.0350	0.0417	−0.0067

Experimental Results

The experimental results are shown in Fig. 1.

At this point it could be seen that the system was not so simple as originally postulated for the full course of the reaction since the concentration of ammonia should have been zero at three moles of ethylene oxide (Fig. 2). The experimental results showed that it approached zero at four moles of ethylene oxide. This would be the case if the ethylene oxide were used up by another reaction, say the formation of tetra-ethanolamine. A search of the literature did not yield much information in this regard (3, 9, 17). Such a reaction is possible by analogy since trimethylamine will react with ethylene oxide to give choline.

In view of the difficulty of interpreting the experimental results more information was sought. First, a static run was conducted using diethanolamine and ethylene oxide. The results were plotted on an ethylene oxide base (Fig. 3). The graph seems to confirm the hypothesis that a fourth compound was formed since the concentration of diethanolamine approaches zero at two moles of ethylene oxide instead of one. It can also be seen that this reaction must be very slow since the curve is very close to the straight line joining one mole of ethylene oxide to one mole of diethanolamine. The second compound would not show up to any appreciable extent until late in

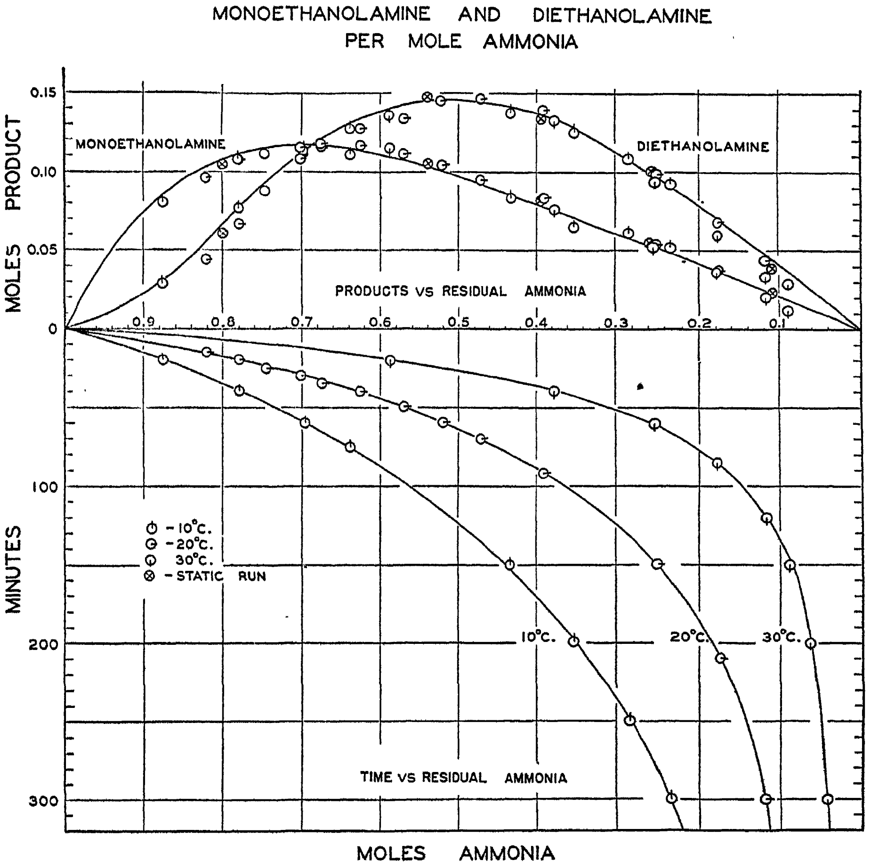


FIG. 1

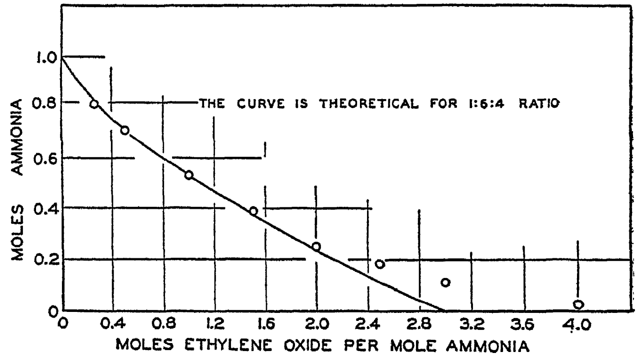


FIG. 2

the reaction. In other words over the early period of a reaction involving ethylene oxide and diethanolamine the ratio at which these two substances would be used up is almost 2 to 1.

Aqueous triethanolamine was mixed with ethylene oxide. Considerable heat was generated, showing that a reaction took place, but attempts to isolate the chloroplatinate of the quaternary ammonium base resulted in the formation of viscous orange oils.

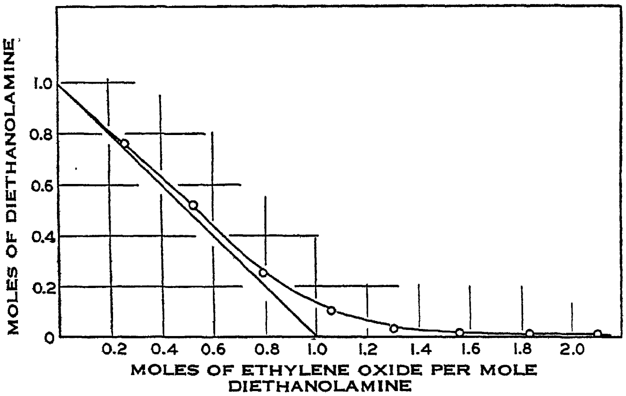


FIG. 3

Finally, the solutions from the static run on ammonia were titrated potentiometrically and the results were plotted as in Fig. 4. This showed the formation of a highly basic substance, probably a quaternary ammonium base.

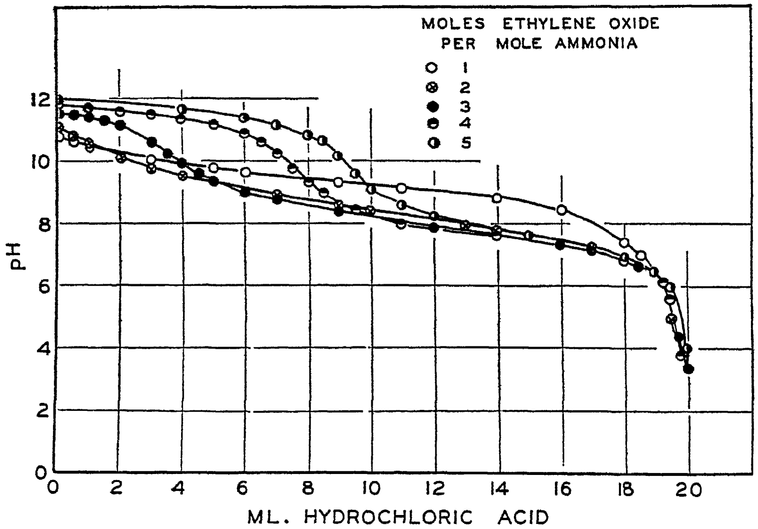


FIG. 4

Controls on the ethanolamines showed them all to be weakly basic. The experiment also indicated that the formation of the quaternary base was not quantitative since not all the weaker bases were converted even at five moles of ethylene oxide per mole of ammonia. In this connection, Fig. 3 shows that the quaternary base does not occur in any appreciable quantity until late in the reaction.

Treatment of Experimental Results

From the foregoing, and from a study of the graphs, it was decided that the over-all reaction, as first postulated, did not give a complete picture of what was taking place in the system. A study of the two graphs (Figs. 2 and 3), plotted on an ethylene oxide base, shows that the effect of the products, other than those postulated, does not exert itself to any appreciable extent until late in the reaction, and the effective rate of formation of these products was slow in comparison with the main reactions. It was, therefore, decided to limit the analysis of the curves to a point where the effect of the secondary products was still small. This was entirely in keeping with the practical aspects of the problem since, at the outset, it was desired only to find the conditions for calculating when the maximum yield of diethanolamine would occur.

The mathematical analysis of the curves was made up to a point where 60% of the ammonia had entered the reaction. All amines other than ammonia, mono-, and diethanolamine were considered to be triethanolamine in the material balance.

TABLE II

Slopes taken from ammonia–time curves in Fig. 1

y_0	10° C.	20° C.	30° C.
0.8	0.004969	0.009466	0.02232
0.6	0.003230	0.005920	0.01460
0.4	0.001838	0.003197	0.00800

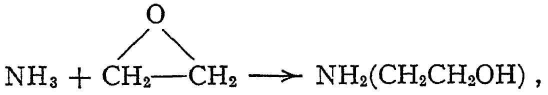
By a process of trial and error the velocity constant ratios $K_1 : K_2 : K_3$ or $1 : \alpha : \beta$ were found to be 1 : 6 : 4 for all temperatures and also for the static run. These calculated curves are represented by the lines in the upper part of Fig. 1 and the points represent experimental values.

There are certain cases where the ratios of the velocity constants could possibly be in the ratio of small whole numbers. In a four step substitution, where the reaction takes place in the ratio of the probability of collision the ratios would be $1 : \frac{3}{4} : \frac{1}{2} : \frac{1}{4}$. Other cases are discussed by R. M. Fuoss (4) in his paper.

Having fixed the ratio of the velocity constants as belonging to a 1 : 6 : 4 system and having assumed that any amines other than ammonia, mono-, and diethanolamine shall be considered as triethanolamine, it becomes possible to evaluate the velocity constants at the temperatures at which the reaction was studied.

The problem was solved by a graphical solution of:

$$\frac{dx}{dt} = k_1(a - x)\ (b - Y)$$



$$NH_3 + \overset{O}{CH_2{-}CH_2} \longrightarrow NH_2(CH_2CH_2OH)\ ,$$

a = original ammonia,
b = original ethylene oxide,
x = ammonia going into reaction.

For 1 : 6 : 4 ratios, calculated points (Table III) give rise to the curves in Fig. 1.

TABLE III

Ammonia present	Ammonia used up	Ethylene oxide used up
y_0	x	Y
0.8	0.2	0.3172
0.6	0.4	0.8402
0.4	0.6	1.5048

Sample Calculation

Ten millilitres of ammonium hydroxide contain 0.0349 equivalents (about 6%, specific gravity 0.973).

	10° C.	20° and 30° C.
Wt. of ammonia solution	9.73	9.73
Wt. of water	10.00	25.00
Wt. of ethylene oxide	6.20	6.20
	25.93 gm.	40.93 gm.

Since for this calculation actual concentrations are required Y must be multiplied by 0.03493/25.93 = 0.001347 for 10° C., and 0.03493/40.93 = 0.0008535 for 20° and 30° C.

The concentration coefficients for $(a - x)$ and dx cancel since they appear on both sides of the equation.

$$b = \frac{6.20}{(44.05)\ (25.93)} = 0.005428 \text{ moles/gm. for } 10^\circ \text{ C.}$$

$$b = \frac{6.20}{(44.05)\ (40.93)} = 0.003444 \text{ moles/gm. for } 20^\circ \text{ C. and } 30^\circ \text{ C.}$$

Solving for k_1 in $\frac{dx}{dt} = k_1\ (a - x)\ (b - Y)$

y_0	k_1 at 10° C.	k_1 at 20° C.	k_1 at 30° C.
0.8	1.243	3.730	8.794
0.6	1.253	3.616	8.921
0.4	1.351	3.699	9.258
	1.282	3.681	8.991 gm./mole/min.

$k = Ze^{-E/RT}$ Arrhenius equation,
k = velocity constant,
E = energy of activation,
Z = collision or orientation factor,

$$E = \frac{(RT'T'')}{(T'' - T')}\, 2.303 \log \frac{k''}{k'}\,.$$

$E_{10^\circ \text{ to } 20^\circ \text{ C.}}$	17,400 cal.
$E_{10^\circ \text{ to } 30^\circ \text{ C.}}$	16,700 cal.
$E_{20^\circ \text{ to } 30^\circ \text{ C.}}$	15,800 cal.
Average	16,600 cal.

In view of the fact that temperature variations did not alter the ratio of the products, the energy of activation is the same for each step and is 16,600 cal. per mole.

An explicit solution for the value of k_1 is possible by substituting for Y in terms of x. It would be tedious and requires finding six roots in this case.

From the values derived, it is possible to solve the problem for any other concentration and temperature conditions by a graphical integration of

$$\frac{dx}{dt} = k_1 (a - x)\ (b - Y)$$

$$k_1 t = \int \frac{dx}{(a - x)\ (b - Y)}$$

k_1 can be found since the energy of activation is known. The values of a, b, and x can be arbitrarily chosen. From Tables II and III sufficient values of $\frac{1}{(a - x)\ (b - Y)}$ could be found to calculate from the equations points to draw a curve over the period 0 to x. By finding the area under this curve the solution for the time of reaction can be readily calculated.

Acknowledgments

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THE KINETICS OF CONSECUTIVE SECOND ORDER REACTIONS[1]

BY C. POTTER[2] AND W. C. MACDONALD[3]

Abstract

A study of consecutive competitive second order reactions is reported. It is shown that identical equations can be obtained by two different approaches. A static method is described where equations are developed by considering the changes brought about in the system by the addition of small quantities of one of the reactants. Equations are also developed from the point of view of kinetics. These equations express the concentrations of the products as functions of the concentration of one of the reactants and the ratio of the velocity constants.

An interesting case of chemical kinetics is that of consecutive competitive second order reactions. One set of theoretical equations was obtained by Fuoss (1) by considering what happens to a system when a differential quantity of one of the reactants is added. Another set of equations can be developed by the method of F. Martin and Fuchs (2) by considering the kinetics of the system. This paper shows that the two methods lead to identical equations.

Method of Differential Material Balances

If the chemical equations are represented by:

$$\begin{aligned} R + S &\longrightarrow RS_1 \\ RS_1 + S &\longrightarrow RS_2 \\ RS_2 + S &\longrightarrow RS_3 \end{aligned}$$

it has been shown that the following set of equations can be developed to describe the system (1).

$$y_1 = \frac{y_0}{1-\alpha}\,[y_0^{\alpha-1} - 1]\,; \quad \alpha \neq 1,$$

$$y_2 = \alpha y_0\left[\frac{y_0^{\beta-1}}{(\alpha-\beta)(1-\beta)} - \frac{y_0^{\alpha-1}}{(\alpha-\beta)(1-\alpha)} + \frac{1}{(1-\alpha)(1-\beta)}\right]; \quad \beta \neq 1,$$

$$3 - Y = Ay_0^{\alpha} + By_0^{\beta} + Cy_0\,,$$

$$A = \frac{1}{1-\alpha} - \frac{\beta}{(\alpha-\beta)(1-\alpha)}\,,$$

$$B = \frac{\alpha}{(\alpha-\beta)(1-\beta)}\,,$$

$$C = 1 - \frac{\alpha}{1-\alpha} + \frac{\alpha\beta}{(1-\alpha)(1-\beta)}\,.$$

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[1] *Manuscript received in original form October 30, 1946, and, as revised, March 28, 1947.*

Contribution from the Department of Chemical Engineering, University of Toronto, Toronto, Ont. Condensed from a portion of a thesis submitted in partial fulfilment of the requirements for the degree of Ph.D.

[2] *Graduate student.*

[3] *Associate Professor.*

The mole fractions of R, RS_1, and RS_2 are represented by y_0, y_1, and y_2. The ratio of the reaction probabilities is $1 : \alpha : \beta$, and Y is the mole fraction of the S constituent.

Kinetic Method

The kinetic method of approach leads to the same conclusions on the assumption that all the reactions are of the second order type.

Let k_1, k_2 and k_3 be the velocity constants,

t = time,
a = initial concentration of R,
b = initial concentration of S,
Y = amount of S which has entered the reaction,
x = amount of R which has entered the reaction,
y_1, y_2, y_3 be the concentration of the products.

A material balance requires that:

$$\begin{aligned} x &= y_1 + y_2 + y_3 \\ Y &= y_1 + 2y_2 + 3y_3. \end{aligned}$$

The rate equations are:

$$\begin{aligned} \frac{dx}{dt} &= k_1(a - x)(b - Y), \\ \frac{dy_1}{dt} &= k_1(a - x)(b - Y) - k_2y_1(b - Y), \\ \frac{dy_2}{dt} &= k_2y_1(b - Y) - k_3y_2(b - Y), \\ \frac{dy_3}{dt} &= k_3y_2(b - Y). \end{aligned}$$

Eliminating dt and integrating between 0 and x gives

$$y_1 = k_1(a - x)\left[\frac{1}{k_2 - k_1} + \frac{1}{k_1 - k_2}\left(\frac{a}{a - x}\right)^{\frac{k_1 - k_2}{k_1}}\right],$$

where

$$\frac{k_2}{k_1} \neq 1.$$

Similarly,

$$y_2 = k_1k_2(a - x)\left[\frac{1}{(k_2 - k_1)(k_3 - k_1)} + \frac{1}{(k_1 - k_2)(k_3 - k_2)}\left(\frac{a}{a - x}\right)^{\frac{k_1 - k_2}{k_1}} + \frac{1}{(k_1 - k_3)(k_2 - k_3)}\left(\frac{a}{a - x}\right)^{\frac{k_1 - k_3}{k_1}}\right].$$

From the symmetry of the equations any y_i can be written down directly. For y_3, if k_4 is zero,

$$y_3 = k_1k_2k_3(a - x)\left[\frac{1}{(k_2 - k_1)(k_3 - k_1)(-k_1)} + \frac{1}{(k_1 - k_2)(k_3 - k_2)(-k_2)}\left(\frac{a}{a - x}\right)^{\frac{k_1 - k_2}{k_1}} + \frac{1}{k_1k_2k_3}\left(\frac{a}{a - x}\right)\right].$$

When $k_i/k_1 = 1$ the integrations lead to logarithmic expressions.

In general it is convenient to use the ratio of the rate constants and to express the concentrations in moles per mole of the original R constituent.

Thus,

$$\begin{aligned}
a &= 1\\
k_2/k_1 &= \alpha\\
k_3/k_1 &= \beta,\\
y_0 &= 1 - x \text{ moles of R per mole of original R used,}\\
y_1 &= \frac{y_0}{1-\alpha}\,(y_0^{\alpha-1} - 1),\\
y_2 &= \alpha y_0\left[\frac{y_0^{\beta-1}}{(\alpha-\beta)(1-\beta)} - \frac{y_0^{\alpha-1}}{(\alpha-\beta)(1-\alpha)} + \frac{1}{(\alpha-1)(\beta-1)}\right],\\
y_3 &= 1 - y_0 - y_1 - y_2,\\
Y &= y_1 + 2y_2 + 3y_3,\\
&= 3 - 3y_0 - 2y_1 - y_2,\\
3 - Y &= Ay_0 + By_0 + Cy_0,\\
A &= \frac{2}{1-\alpha} + \frac{\alpha}{(1-\alpha)(\beta-\alpha)} \equiv \frac{1}{1-\alpha} - \frac{\beta}{(\alpha-\beta)(1-\alpha)},\\
B &= \frac{\alpha}{(1-\beta)(\alpha-\beta)},\\
C &= 3 + \frac{2}{\alpha-1} + \frac{\alpha}{(\alpha-1)(\beta-1)} \equiv 1 - \frac{\alpha}{1-\alpha} + \frac{\alpha\beta}{(1-\alpha)(1-\beta)}.
\end{aligned}$$

Thus it is seen that the kinetic and static approaches lead to the same equations for the system.

The next question that arises is: what is the significance of $\alpha = k_2/k_1$ and $\beta = k_3/k_1$, where α and β are defined as the reaction probabilities?

Writing the Arrhenius equation as $k = z\,e^{-E/RT}$, where z includes all the requirements that the reacting molecules must have other than those of energy, k is the rate constant, and E the energy of activation.

$$\begin{aligned}
k_1 &= z_1\,e^{-\frac{E_1}{RT}},\\
k_2 &= z_2\,e^{-\frac{E_2}{RT}},\\
\alpha &= \frac{k_2}{k_1} = \frac{z_2}{z_1}e^{\frac{(E_1-E_2)}{RT}}.
\end{aligned}$$

When the successive reactions make similar replacement of bonds, the energies of activation may be nearly equal for each step. In this case

$$1 : k_2/k_1 : k_3/k_1 = 1 : z_2/z_1 : z_3/z_1 = 1 : \alpha : \beta$$

and the equations governing y_i and Y will be independent of temperature. This would indicate that the difference in reaction probabilities is due only to the orientation requirements of the reacting species of molecules.

On the other hand, if each step has a different energy of activation, then the values of α and β will no longer be independent of temperature:

$$\alpha = \frac{k_2}{k_1} = \frac{z_2}{z_1} e^{\frac{E_1 - E_2}{RT}} ,$$

$$\alpha' = \frac{k_2'}{k_1'} = \frac{z_2}{z_1} e^{\frac{E_1 - E_2}{RT'}} ,$$

$$\frac{\alpha}{\alpha'} = e^{\frac{E_1 - E_2}{R} \left(\frac{T' - T}{TT'}\right)} .$$

It is of interest to note that the equations governing the intermediates, y_1, and y_2, depend only on the way in which these products are formed and disappear, and not on the number of steps involved after their disappearance. On the other hand, this reasoning does not hold for the equations governing the disappearance of R and S, nor for the formation of the final product. Thus if the values of the intermediate y_i's are plotted against y_0 the shapes of the curves do not depend on the number of steps involved.

In order to determine the ratio of the rate constants, it is not necessary to find the rates of reaction but merely to set up several experiments in which a fixed quantity of R is reacted with different quantities of S. Analysis of the resulting mixtures will yield considerable information. When the values of y_i are plotted against y_0 it is possible to tell whether the reaction proceeds as postulated by the way in which the experimental curves fit the family of theoretical curves. The ratio of the velocity constants can be found by fitting the experimental results to theoretical curves. If the experimental curves shift with temperature, then it will be realized that the energy of activation is not the same for each step.

When R is ammonia and the reaction involves substituting S radicals for hydrogen, there may be some doubt whether a quaternary ammonium base is formed, as in the formation of ethanolamines (3). By plotting the experimental results for the y_i's against Y it will be realized that if they approach zero at $Y = 4$ moles, then a quaternary ammonium base is likely to have been formed, but on the other hand if they approach zero at $Y = 3$ moles, then it is not likely that a fourth amine is present.

If it is desired to find the absolute values of the velocity constants, then it will be necessary to run a series of kinetic experiments. From the results, the ratios of the velocity constants may be found as before. By plotting the values of x against time t, the value of k_1 can be found from $\frac{dx}{dt} = k_1(a - x)(b - Y)$. In general a graphical solution will be necessary since an explicit solution of the above equation except in special cases is very cumbersome.

Acknowledgment

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Fractionation of the Reaction Product of Linseed Oil and Glycerol

This paper presents the results of attempts to separate the reaction product of linseed oil and glycerol into fractions of different unsaturation, which may be useful in the production of ester-type resins and other industrial applications (4).

Reaction Between Linseed Oil and Glycerol.—The literature on the reaction between glyceride oils and glycerol has been reviewed by Goldsmith (4); Blagonravova *et al.* (2) and Feuge and Bailey (3) have published papers on the composition of the reaction product.

The reaction was carried out as follows: the amount of B.P. glycerol shown in Table I and 300 gm. alkali-refined linseed oil (iodine no. = 185.0, saponification no. = 197.0, average number of double bonds per fatty acid radical = 2.08) were placed in a 1 litre Pyrex three-necked flask, fitted with thermometer, stirrer, and air-cooled reflux condenser. The mixture was heated to 240° C., 0.3 gm. calcium acetate monohydrate added, and the temperature maintained at 240° C. for one hour. The mixture was allowed to cool to room temperature and the two resulting liquid layers separated, the lower layer consisting of glycerol and a trace of ester, and the upper layer consisting of the partial ester and some free glycerol. The upper layer was used as obtained for the subsequent fractionation experiments.

Table I shows some of the properties of representative ester layers obtained by using different proportions of glycerol, the average number of double bonds per fatty acid radical being indicated by the symbol N.

TABLE I

Type	Glycerol, gm.		Ester layer			
	Used	Recovered	Weight, gm.	Iodine No.	Saponification No.	N
A	300	209.1	377.5	145.5	157.0	2.05
B	225	134.8	374.1	144.0	157.2	2.03
C	150	64.3	376.9	143.7	159.1	2.00
D	75	10.6	361.7	149.2	162.3	2.03
E	45	2.1	336.7	159.6	173.7	2.03

For economic reasons it would be imperative that the glycerol recovered be re-used in subsequent reactions, and in order to ascertain that on continued re-use no accumulation of ether-type compounds in the glycerol took place,

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the hydroxyl content of the recovered glycerol from Type *C* reactions was determined by the method of Ogg, Porter, and Willits (6). It was found that the original glycerol had hydroxyl content = 54.7%; after being used two and three times the values were 54.0% and 55.2% respectively.

Fractionation of the Reaction Product.—Attempts were made to separate the reaction product into fractions of different degree of unsaturation by three methods, involving (*a*) distribution in two-phase liquid systems, (*b*) fractional crystallization of the reaction product, and (*c*) fractional crystallization of a solution of the reaction product. No appreciable separation was obtained by Method (*a*), but a certain degree of separation resulted using Method (*b*). Using crystallization temperatures from 25° to 5° C., solid fractions were obtained ranging from 10 to 40% by weight of the starting sample, and with a value for $N = 1.7 \pm 0.1$. Using Method (*c*), however, an appreciable degree of separation was obtained. The general procedure was as follows: a sample of the reaction product was dissolved in a solvent, and the solution allowed to stand at the temperatures noted for from 24 to 48 hr., until crystallization was apparently complete. The solid fraction was separated by filtration through Whatman No. 4 filter paper and its characteristics determined, from which those of the liquid fractions may be calculated. The results are summarized in Table II, in which the weights of the solid fractions are those obtainable from 100 gm. of the reaction product.

TABLE II

Type	Temp., °C.	Solvent	Amount, gm.	Solid fraction			
				Weight, gm.	Iodine No.	Saponification No.	N
A	5	Carbon tetrachloride	100	8.7	68.8	140.5	1.08
A	5	Benzene	100	8.5	93.5	150.0	1.38
A	5	Chloroform	100	20.0	103.6	147.4	1.56
A	5	Methanol	100	13.8	118.0	161.0	1.62
A	5	95% methanol, 5% water	100	16.3	119.6	160.9	1.65
A	5	Ethyl acetate	100	19.2	102.8	137.4	1.66
A	5	95% acetone, 5% water	100	19.0	116.8	154.1	1.68
A	5	Acetone	100	15.5	115.2	150.0	1.70
A	5	Diethylether	100	17.0	116.6	138.0	1.87
C	5	Carbon tetrachloride	100	11.2	74.3	150.1	1.10
D	5	"	100	14.0	104.6	159.0	1.46
E	5	"	100	18.8	125.7	166.6	1.67
A	5	"	75	8.9	78.6	148.2	1.17
A	5	"	50	9.8	97.2	159.6	1.35
A	5	"	25	32.6	124.1	157.0	1.75
A	0	"	100	13.3	83.4	143.2	1.29
A	0	"	75	17.7	102.5	147.9	1.53
A	− 5	"	100	23.6	95.2	137.0	1.54
A	−10	"	150	20.4	98.4	123.1	1.77

In order to determine the range of this method of fractionation, similar crystallizations were carried out, using as starting material samples of Type *A* reaction products which had already been fractionated to some extent. The results are summarized in Table III, in which the weights of the solid fractions are those obtainable from 100 gm. of the starting material.

TABLE III

Starting material			Solvent	Temp. ° C.	Solid fraction			
Iodine No.	Saponification No.	*N*			Weight, gm.	Iodine No.	Saponification No.	*N*
155.6	157.9	2.18	30 gm. CH_3OH	−20	0	—	—	—
149.4	156.1	2.12	10 gm. "	−10	30.0	135.0	152.0	1.96
153.4	161.6	2.10	100 gm. CCl_4	−20	55.5	143.5	156.2	2.04
151.6	162.0	2.07	50 gm. "	−10	48.4	148.4	162.6	2.02
146.0	157.9	2.05	50 gm. "	− 5	17.0	127.6	152.5	1.85
120.9	154.0	1.74	150 gm. "	25	28.2	94.0	154.7	1.34
94.0	154.7	1.34	200 gm. "	30	46.1	60.0	143.0	0.93
60.0	143.0	0.93	300 gm. "	30	40.0	18.2	134.4	0.30
46.6	140.0	0.74	400 gm. "	30	50.8	12.0	116.2	0.22

Discussion.—Although fractional crystallization without a solvent is a relatively inefficient method of separation, it would require a minimum of equipment in practice, and the fractions produced might serve as starting materials for crystallization from a solvent.

It is interesting to note that fractionation takes place with respect to fatty acid content as well as unsaturation, since fractions of low unsaturation also have a low saponification number.

It is suggested that the ideas outlined here might be adaptable to drying oils other than linseed oil, especially those that contain comparatively large amounts of fatty acids of low unsaturation, such as soya bean oil.

Analytical Methods.—The iodine numbers of the fractions were determined by the Hanus method (1); the saponification numbers were determined by the decigram procedure described by Marcali and Rieman (5); from these data the average number of double bonds per fatty acid radical was calculated.

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J. G. BRECKENRIDGE
J. H. E. HERBST

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PRODUCTION AND PROPERTIES OF 2,3-BUTANEDIOL

XXIII. CONDENSATION OF THE ISOMERIC 2,3-BUTANEDIOLS WITH ETHYL ACETOACETATE[1]

BY A. C. NEISH[2]

Abstract

levo-2,3-Butanediol will condense with ethyl acetoacetate in the presence of hydrochloric acid to give the ethyl ester of *levo*-2,4,5-trimethyl-2-carboxymethyl-1,3-dioxacyclopentane (I) (yield 48%) from which the free acid may be obtained. If *p*-toluenesulphonic acid is used as the catalyst and the condensation is carried out in boiling butanol with continuous removal of water, the butyl ester of (I) is obtained (yield 87%). Compounds described for the first time are *levo*-, *dl*-, and *meso*-2,4,5-trimethyl-2-carboxymethyl-1,3-dioxacyclopentanes, their *n*-butyl and *p*-bromophenacyl esters (melting points 74.5°, 76°, and 76° C., respectively) and the ethyl ester of the *levo*-isomer.

Previous work has shown that one of the most striking chemical properties of 2,3-butanediol is the ease with which it forms cyclic acetals and ketals (1, 4); this is particularly true of the *levo*-isomer. This paper describes the cyclic ketals of 2,3-butanediol obtained through reactions involving esters of acetoacetic acid, and thus serves to extend our knowledge of the chemistry of 2,3-butanediol.

Acetoacetic acid is too unstable to condense directly with 2,3-butanediol but the commercially available ethyl ester will react readily at room temperature, in the presence of hydrochloric acid, to give the ethyl ester of 2,4,5-trimethyl-2-carboxymethyl-1,3-dioxacyclopentane. The yield obtained (*levo*-isomer) was only 48% of the theory, partly because the reaction is reversible but also because of side reactions such as hydrolysis and decarboxylation. If the reaction is conducted in boiling benzene using *p*-toluenesulphonic acid as a catalyst and removing the water as it forms the yield is slightly poorer, probably because of loss of the ethyl ester groups due to hydrolysis or alcoholysis. A good yield of the butyl ester of this ketal can be obtained, however, by carrying out the condensation in an excess of boiling *n*-butanol. The butanol is allowed to distil slowly from the reacting mixture in order to remove the water. In this way yields up to 87% of the theory were obtained. The isomeric *levo*-, *dl*-, and *meso*-butyl esters of 2,4,5-trimethyl-2-carboxymethyl-1,3-dioxacyclopentane were prepared in this way. These can be

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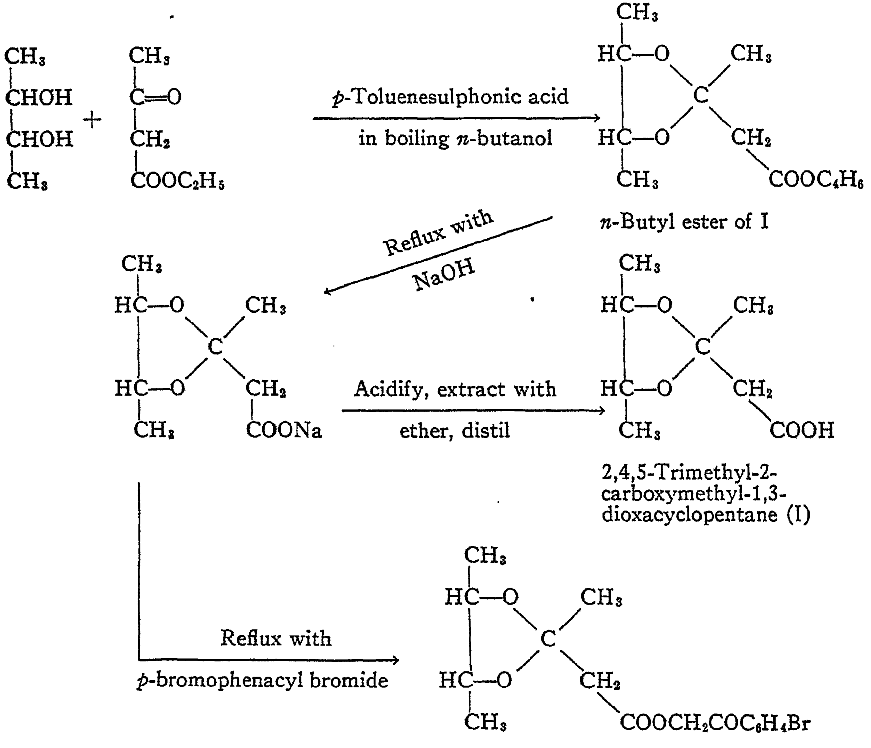
[2] *Biochemist, Industrial Utilization Investigations.*

readily converted into the corresponding sodium salts by alkaline hydrolysis with sodium hydroxide. The free acids may be obtained from the sodium salts by acidification and extraction with ether. The yields are only 60 to 75%, probably because of hydrolysis of the dioxacyclopentane ring on acidification. The sodium salts can be converted to the crystalline *p*-bromophenacyl esters by refluxing with *p*-bromophenacyl bromide (75% yield based on butyl ester). These crystalline esters are very similar to each other in solubility and melting point and hence are not suitable for identifying the different isomeric 2,3-butanediols in a mixture. The above mentioned chemical transformations are shown in the following scheme. This has been realized with *levo*-, *dl*-, and *meso*-2,3-butanediol; all products have been purified and characterized except the sodium salts.



Experimental

Materials and Methods

The *l*-, *dl*-, and *meso*-2,3-butanediols were obtained by suitable purification of the 2,3-butanediols formed by bacterial fermentation as described below. The ethyl acetoacetate was obtained by redistilling the technical grade material obtained from the Certified Chemical Company. The *p*-bromophenacyl bromide, propionaldehyde, and *p*-toluenesulphonic acid (monohydrate) were Eastman chemicals, and the *n*-butanol, Merck's Reagent Grade.

The equivalent weights of the acids were determined by dissolving a weighed amount (2 gm.) in methanol and titrating to the phenolphthalein end-point with aqueous standard sodium hydroxide. The equivalent weights of the esters were determined by refluxing a weighed sample (2 gm.) with methanol and excess aqueous normal sodium hydroxide for two hours, allowing to cool overnight and then titrating to the phenolphthalein end-point with normal hydrochloric acid. Melting points were determined using an apparatus similar to that of Dennis and Shelton (2), which gives corrected melting points with an accuracy of 0.5° C. Bromine determinations were made using Umhoeffer's method (5), while carbon and hydrogen were determined by the well known method of Liebig. Refractive indices were determined by means of an Abbé refractometer.

levo-2,3-Butanediol

This isomer is easily obtained since *Aerobacillus polymyxa* produces it to the practical exclusion of the *meso*- and *dextro*-isomers (3). The material obtained from the Fermentations Pilot Plant, operated by this Division, was redistilled to give a colourless liquid, $[\alpha]_D^{25} = -12.84°$. This was used without further purification although it probably contains a small amount of water.

racemic-2,3-Butanediol

This can be made synthetically starting with *n*-butanol (6) but it is easier to prepare it by mixing *levo*- and *dextro*-2,3-butanediols prepared by fermentation. No organism is known that produces pure *dextro*-2,3-butanediol, but *Aerobacter aerogenes* gives a mixture of the *dextro*- and *meso*-isomers, which can be readily separated. This separation can be effected by direct distillation but since the isomers have boiling points only 3° to 4° C. apart it is advisable first to convert the mixture to the isomeric 2,2,4,5-tetramethyl-1,3-dioxacyclopentanes, which have boiling points separated by 8° to 9°.C. This was done by condensing the 2,3-butanediol produced by *A. aerogenes*, $[\alpha]_D = +1.0$, with an equimolecular amount of acetone as previously described (4) for the *levo*-isomer. Owing to the relatively poor reaction obtained with the *meso*-isomer it is necessary to use 75 ml. of concentrated sulphuric acid per litre of diol in order to obtain two phases in a reasonable time. The top layer on distillation through a column packed with glass helices followed by redistillation through a Stedman column (about 24 theoretical plates) gave a fraction boiling between 109.5° and 110.5° C. This is chiefly *dextro*-2,2,4,5-tetramethyl-1,3-dioxacyclopentane. After separation of a small intermediate fraction the *meso*-isomer was obtained boiling at 119° C. The total yield of crude ketals (top layer) was only about 25% owing to the poor reactivity of the *meso*-2,3-butanediol but one-quarter of this was the *dextro*-isomer. This shows the *meso*-isomer to be less reactive with acetone than the *dextro*. The observed rotation of this isomer was only + 15.0° instead of +19.1° as expected by comparison with the *levo*-isomer (4). It is probable that the crude 2,3-butanediol used contained some of the *levo*-isomer, picked up in the pilot plant when it was distilled through columns previously used for *levo*-2,3-butanediol. This view is substantiated by its rotation, which is a little lower than that expected.*

The fraction, $[\alpha]_D^{25} = +15.0°$, was mixed with sufficient *levo*-2,2,4,5-tetramethyl-1,3-dioxacyclopentane to give an optically inactive solution. The racemic mixture thus obtained (598 ml.) was hydrolysed by refluxing with one litre of water containing 50 ml. of concentrated hydrochloric acid. The acetone was allowed to distil out through a 2 ft. column packed with glass helices. When the temperature reached 100° C. the residual solution was cooled, then neutralized with sodium hydroxide pellets to pH 4 to 5. The water was then distilled out and the residue separated from the sodium chloride by extraction with ether. Fractional distillation of the extract gave 340 ml. of *racemic*-2,3-butanediol boiling at 127° C. (124 mm.). This fraction had a refractive index of 1.4310 at 25° C. and a melting point of 7.0° to 7.5° C. These properties are in good agreement with those of the synthetic product (6). The yield on hydrolysis is about 95%.

meso-2,3-Butanediol

This can be prepared by hydrolysis of the *meso*-2,2,4,5-tetramethyl-1,3-dioxacyclopentane obtained as described above. However, since *meso*-2,3-butanediol does not condense readily with ketones but reacts vigorously with aldehydes, it was decided to purify some of the crude *A. aerogenes* diol by reaction with propionaldehyde. One litre of the 2,3-butanediol, $[\alpha]_D = +1.0°$ was mixed with 800 ml. of Eastman's propionaldehyde and 5 ml. of concentrated hydrochloric acid added. The mixture heated spontaneously to 45° C. and two phases formed in a few minutes. It was stirred and allowed to cool overnight. The small lower layer was discarded; the top layer was washed with saturated sodium bicarbonate, filtered through anhydrous sodium sulphate and then distilled through a 2 ft. column packed with glass helices. Some diphasic azeotrope (40 ml. boiling at 89° C.) was obtained but the major fraction was a colourless liquid boiling at 125° to 133° C. with the observed rotation varying from + 1.0° to + 0.3°. The yield was 1400 ml. or 93%. This mixture of the *dextro*- and *meso*-2-ethyl-4,5-dimethyl-1,3-dioxacyclopentanes was carefully fractionated through a Stedman column and 480 ml. finally obtained with $[\alpha]_D = +0.06°$ and a boiling range 133.5° to 134.5° C. The lowest boiling fraction (126° to 127° C.) had $[\alpha]_D = +6.7°$. Most of the material was obtained as intermediate fractions. The fraction with the lowest rotation (415 ml.) was hydrolysed with dilute hydrochloric acid as described above for the *racemic* acetone derivative. Fairly pure *meso*-2,3-butanediol (250 gm.) was obtained as a white solid (m.p. 32° to 33° C.). The melting point of the highly purified diol is 34.4° C. (6).

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* *The presence of dl-2,3-butanediol in this sample has recently been proved by isolation as the di-p-nitrobenzoate.*

Ethyl ester of levo-2,4,5-trimethyl-2-carboxymethyl-1,3-dioxacyclopentane

Ethyl acetoacetate (2 moles) and *levo*-2,3-butanediol (2 moles) were mixed, treated with 10 ml. of concentrated hydrochloric acid, and allowed to stand overnight. Then 200 ml. of ethyl ether was added to the diphasic product and the ethereal layer washed with 100 ml. of saturated sodium bicarbonate. After filtering through anhydrous sodium sulphate the ether extract was distilled through a column of glass helices. About 35 gm. of ethyl acetoacetate was recovered but the main fraction was a colourless liquid boiling at 114° C. (42 mm.). This proved to be the ethyl ester of the cyclic ketal formed between acetoacetic acid and *levo*-2,3-butanediol as expected. (Yield 48%). Calc. for $C_{10}H_{18}O_4$: C, 59.38; H, 8.97%; equiv. wt., 202.2. Found: C, 59.2, 59.3; H, 8.90, 8.85%; equiv. wt., 201, 203. $n_D^{25} = 1.4230$; $d_4^{25} = 1.0065$; $[\alpha]_D^{25} = -15.21°$. Molar refraction: calc., 51.26; found, 51.17.

A small amount (30 gm.) of a liquid boiling at 40° C. (300 mm.) with a camphor-like odour was obtained. This was probably the acetone derivative resulting from hydrolysis and decarboxylation of the ethyl acetoacetate. An attempt to obtain a high yield by using *p*-toluenesulphonic acid and removing the water by azeotropic distillation with benzene was unsuccessful. Owing to hydrolysis of the ester groups and possibly esterification with the diol, the yield obtained in this way was only 43%. However, a good yield could be obtained by carrying out the reaction in an excess of boiling butanol; in this case the main product is the butyl ester as shown next.

Butyl ester of levo-2,4,5-trimethyl-2-carboxymethyl-1,3-dioxacyclopentane

Ethyl acetoacetate (2 moles), *l*-2,3-butanediol (2 moles), and *n*-butanol (4 moles) were refluxed in an apparatus provided with a controlled take-off. The butanol was drawn off till the temperature of the vapour reached 115° C. A solution of 2 gm. of *p*-toluenesulphonic acid monohydrate in 500 ml. of butanol was added and 550 ml. then distilled off over a period of two hours as the temperature of the vapour rose gradually to 120° C. The reaction mixture was cooled overnight, then poured into a separatory funnel, washed with saturated sodium bicarbonate solution, filtered through anhydrous sodium sulphate, and fractionated through a column of glass helices. The butyl ester was the only product obtained in any appreciable quantity. (Yield 87%.) It is a colourless liquid boiling at 159° C. (58 mm.). Calc. for $C_{12}H_{22}O_4$: C, 62.61; H, 9.64%; equiv. wt., 230.3. Found: C, 62.4, 62.5; H, 9.45, 9.59%; equiv. wt., 228, 229; $n_D^{25} = 1.4270$; $d_4^{25} = 0.9781$; $[\alpha]_D^{25} = -13.39°$; molar refraction: calc., 60.47; found, 60.44.

Butyl ester of dl-2,4,5-trimethyl-2-carboxymethyl-1,3-dioxacyclopentane

racemic-2,3-Butanediol (2 moles) and ethyl acetoacetate (2 moles) were mixed with butanol (650 ml.) and *p*-toluenesulphonic acid monohydrate (2 gm.). During a period of 4½ hr., 610 ml. of butanol was distilled from the reaction mixture. It was cooled overnight, then washed, dried, and distilled as described above. A liquid boiling at 132° to 133° C. (100 mm.)

was obtained (35 gm.) but the main product was a liquid boiling at 157° C. (55 mm.). The former is probably the ethyl ester (yield 8%) while the latter was proved to be the butyl ester (yield 64%). The properties of the butyl ester were found to be as follows. Calc. for $C_{12}H_{22}O_4$: C, 62.61; H, 9.64%; equiv. wt., 230.3. Found: C, 62.5, 62.6; H, 9.62, 9.88%; equiv. wt., 227, 228. $n_D^{25} = 1.4269$; $d_4^{25} = 0.9790$. Molar refraction: calc., 60.47; found, 60.39.

Butyl ester of meso-2,4,5-trimethyl-2-carboxymethyl-1,3-dioxacyclopentane

Ethyl acetoacetate (2 moles) and *meso*-2,3-butanediol were condensed in boiling butanol as described above for the *levo*-isomer. The butyl ester of the cyclic ketal formed between acetoacetic acid and *meso*-2,3-butanediol was the only product obtained in any appreciable amount. (Yield 74%). It is a colourless liquid boiling at 164° C. (58 mm.). Calc. for $C_{12}H_{22}O_4$: C, 62.61; H, 9.64%; equiv. wt., 230.3. Found: C, 62.4, 62.5; H, 9.54, 9.60%; equiv. wt., 228, 229. $n_D^{25} = 1.4320$; $d_4^{25} = 0.9914$; molar refraction: calc., 60.47; found, 60.24.

levo-2,4,5-Trimethyl-2-carboxymethyl-1,3-dioxacyclopentane

This acid was obtained by saponification of its ethyl ester (0.5 mole) by refluxing with 50 ml. of methanol and 110 ml. of 5 *N* sodium hydroxide for one hour. After standing 16 hr. at room temperature the hydrolysate was adjusted to pH 10 and concentrated on a steam-bath to remove methanol. It was cooled, acidified with 10% excess of 10 *N* sulphuric acid and extracted with ether (twice), the extract washed with water, filtered through anhydrous sodium sulphate, and distilled. The acid was obtained as a colourless, viscous liquid with a faint camphor-like odour, boiling at 129° C. (5 mm.). (Yield 74%). It was redistilled through a short Vigreux column and its properties determined. Calc. for $C_8H_{14}O_4$: C, 55.15; H, 8.10%; equiv. wt., 174.2. Found: C, 55.1, 55.0; H, 8.08, 8.12%; equiv. wt., 175, 176. $n_D^{25}=1.4352$; $d_4^{25} = 1.0856$; $[\alpha]_D^{25} = -18.40°$; molar refraction: calc., 42.04; found, 41.88.

dl-2,4,5-Trimethyl-2-carboxymethyl-1,3-dioxacyclopentane

This acid was obtained by saponification of its butyl ester (0.5 mole) by refluxing with 100 ml. of methanol and 110 ml. of 5 *N* sodium hydroxide for $1\frac{1}{2}$ hr. The hydrolysate was cooled overnight, diluted with 500 ml. of water, acidified with 80 ml. of 7.5 *N* sulphuric acid and immediately extracted with 1200 ml. of ethyl ether used in three equal portions. The extract was washed once with water, filtered through anhydrous sodium sulphate, and distilled.

The chief product was 53 gm. of the crude acid (equiv. wt., 194) boiling at 127° C. (3 mm.). This contains some lower-boiling, neutral substance which was removed by fractionation through a short Vigreux column to give the pure acid boiling at 131° C. (6 mm.). (Yield 57%, calculated on acid in crude fraction.) Calc. for $C_8H_{14}O_4$: C, 55.15; H, 8.10%; equiv. wt., 174.2. Found: C, 55.1, 55.0; H, 8.10, 8.14%; equiv. wt., 177, 178. $n_4^{25} = 1.4350$; $d_4^{25} = 1.0795$; molar refraction: calc., 42.04; found, 42.11.

meso-2,4,5-Trimethyl-2-carboxymethyl-1,3-dioxacyclopentane

This acid was prepared by saponification of its butyl ester following the same procedure as that just given for the racemic mixture. It was obtained as a liquid boiling at 138° C. (5 mm.). The crude acid had an equivalent weight of 268 owing to the presence of some neutral substance. The analytically pure material obtained represented a yield of only 10% although a 68% yield of this acid was obtained (calculated on acid in high boiling fraction). Calc. for $C_8H_{14}O_4$: C, 55.15; H, 8.10%; equiv. wt., 174.2. Found: C, 55.1, 55.2; H, 8.10, 8.14%; equiv. wt., 176, 178. $n_D^{25} = 1.4415$.

p-Bromophenacyl Esters of the Isomeric 2,4,5-Trimethyl-2-carboxymethyl-1,3-dioxacyclopentanes

These were prepared from the corresponding butyl esters by saponification, followed by treatment of the sodium salt, thus obtained, with *p*-bromophenacyl bromide. The butyl ester (4 gm.) was treated with an excess of normal sodium hydroxide (20 ml.) and methanol (20 ml.), and refluxed for one hour. After allowing the reaction mixture to cool overnight it was titrated with normal hydrochloric acid till just acid to phenolphthalein. An equimolecular amount of *p*-bromophenacyl bromide was then added, the mixture refluxed for one hour, cooled, diluted with two volumes of water, and placed in a refrigerator. A greenish oil separated and then solidified. This was recrystallized from methanol to give yellowish crystals: m.p., 65° to 68° C. The yield at this stage was 70 to 75%. Two or three further recrystallizations from Skellysolve B gave pure colourless crystals. The *levo*-ester melts at 74.5° C. and the *dl*- and *meso*-ester both melt at 76° C. These compounds do not show much depression of the melting point when mixed; the last two when mixed in equal proportions give a mixture melting at 74° C., the lowest melting point observed. Calc. for $C_{16}H_{19}O_5Br$: C, 51.76; H, 5.16; Br, 21.53%. Found (*levo*-isomer): C, 51.7, 51.6; H, 5.19, 5.24; Br, 21.61, 21.55%. (*dl*-isomer): C, 51.5, 51.6; H, 5.28, 5.20; Br., 21.58, 21.52%. (*meso*-isomer): C, 51.7, 51.6; H, 5.28, 5.18; Br, 21.47, 21.51%.

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THE HYDROLYSIS AND POLYMERIZATION OF CYANOGEN CHLORIDE IN THE PRESENCE OF HYDROGEN CHLORIDE[1]

BY A. B. VAN CLEAVE[2] AND H. E. MITTON[3]

Abstract

Cyanogen chloride reacts quantitatively with water in the presence of hydrochloric acid according to the equation: $CNCl + 2H_2O \rightarrow CO_2 + NH_4Cl$. As the percentage of hydrochloric acid is reduced towards zero, the rate of hydrolysis at 30° C. becomes exceedingly slow. The rate of hydrolysis, as indicated by the pressure increase, shows an increase with time which is particularly marked when the concentration of hydrogen chloride is less than 1%. This apparent autocatalytic effect is not due to the accumulation of solid ammonium chloride. A polymerization reaction, the rate of which is increased by the addition of dry hydrogen chloride, proceeds simultaneously with the hydrolysis reaction. Pure cyanogen chloride shows little or no tendency to polymerize at 30° C. Carbon dioxide has been shown to be quite soluble in liquid cyanogen chloride and an explanation has been suggested for the form of the pressure vs. time curves obtained in studying the acid catalyzed hydrolysis and polymerization of cyanogen chloride.

Introduction

It is well known that the stability of cyanogen chloride is greatly influenced by the presence of acid impurities (2). These impurities appear to have two effects: first, to catalyze the reaction of cyanogen chloride with water and, second, to catalyze the polymerization to cyanuric chloride $(CNCl)_3$ (1, 2, 5). The present work is concerned with the re-establishment of the products of the acid catalyzed hydrolysis and with a study of the factors affecting the rate of this reaction and the polymerization reaction.

It has been shown (4) that a considerable pressure of carbon dioxide is produced in closed systems consisting of cyanogen chloride, water, and small amounts of acid impurities. It is also known that part of the white solid that separates out from crude cyanogen chloride is ammonium chloride. These facts suggest that the over-all hydrolysis reaction might be represented by the equation:

$$CNCl + 2H_2O \longrightarrow CO_2 + NH_4Cl\ . \qquad (1).$$

This reaction can be shown to be entirely probable from a thermodynamic standpoint, the estimated equilibrium constant at 20° C. being of the order of 10^{48}.

Experimental

1. *Hydrolysis Experiments*

With the view of determining whether Equation (1) represented the over-all hydrolysis reaction, an apparatus (Fig. 1) was designed and constructed to follow the course of the reaction by measuring the pressure change and analysing the products.

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Contribution from the Department of Chemistry, University of Saskatchewan, Saskatoon, Sask., with financial assistance from the National Research Council of Canada.

[2] *Associate Professor of Chemistry.*

[3] *Graduate student. Holder at the time of a Bursary and Studentship under the National Research Council of Canada.*

Crude cyanogen chloride (American Cyanamid Company) was filtered to remove polymer and solid ammonium chloride, and then purified by fractional crystallization (6). Liquid cyanogen chloride was about 80% frozen and the remaining liquid poured off. The solid was then melted and the process repeated, until a product showing a constant freezing point of −6.9° C. was obtained. Cyanogen chloride purified in this way proved to be quite stable over considerable periods of time. The purified liquid in *A* (Fig. 1) was allowed to vaporize into the previously calibrated and evacuated measuring vessel, *B*. Assuming that the vapour of cyanogen chloride obeys the ideal gas laws at 20° C. and pressures less than 1 atm., the amount of cyanogen chloride transferred from *A* to *B* could be calculated. When sufficient cyanogen chloride vapour had accumulated in *B*, stopcock *C* was closed and *D* and *E* opened to allow the vapour to freeze out in the evacuated reaction vessel, *F*, which was immersed in a dry ice – acetone freezing mixture. The amount of cyanogen chloride remaining in the vessel *B* was negligible as its vapour pressure at −78° C. is less than 1 mm. of mercury. When the transfer was complete the stopcocks *D* and *E* were closed (*E* being clamped) and the reaction vessel and attached manometer removed and placed in a constant temperature bath. When equilibrium was established, the vapour pressure was noted as an additional check on the purity of the cyanogen chloride. The reaction vessel was then cooled until the vapour pressure of the cyanogen chloride was somewhat less than atmospheric, when the desired amount of standard hydrochloric acid solution was admitted through the tap, *G*, from the calibrated capillary burette, *H*. After mixing the reactants by shaking, the reaction vessel was re-immersed in the constant temperature bath and the course of the reaction followed by noting the pressure at intervals. In all cases the pressure increased up to a maximum where readings were discontinued in the initial experiments.

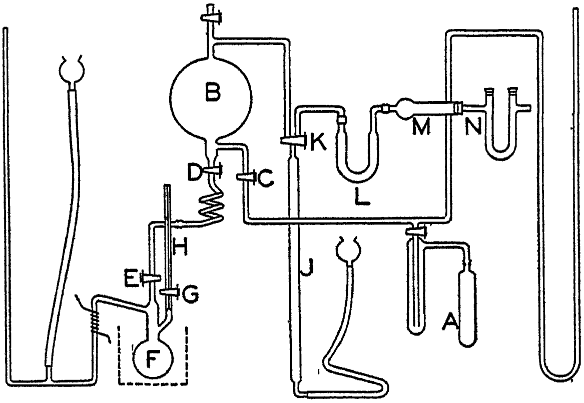

FIG. 1. *Diagram of apparatus.*

The next step was to analyse the products qualitatively and quantitatively. Condensable vapours in the reaction vessel were frozen out with a dry ice – acetone bath. The reaction vessel was again attached to the evacuated measuring bulb, *B*, and stopcocks *D* and *E* opened, allowing the uncondensed gases to flow until equilibrium was attained. Stopcock *D* was then closed and the gas in the measuring chamber analysed. The gas in *B* still contained a small amount of cyanogen chloride which could be detected by its odour and lachrymal property. Some of the gas was bubbled through a saturated barium hydroxide solution, and a heavy white precipitate resulted. This precipitate was filtered out, washed and dried, and analysed gravimetrically for barium. It yielded 68% of barium, whereas the theoretical value for barium carbonate is 69.5%. This indicated that a considerable amount of carbon dioxide had been formed during the reaction.

A quantitative analysis of the gas was done by attaching a mercury filled, calibrated gas burette, *J* (Fig. 1), to the bulb, *B*, by the three-way tap, *K*. This made it possible to withdraw measured portions of the gas and transport them to the gas absorber, *L*, which contained dilute (chloride free) sodium hydroxide solution. Attached to the gas absorber was a calcium chloride tube, *M*, to absorb any water that might be lost from the sodium hydroxide solution during the absorption process. The tubes *L* and *M* were weighed before and after absorption. A tube, *N*, containing a mixture of soda lime and calcium chloride served to protect the absorption train from atmospheric carbon dioxide and water vapour. When absorption was complete the solution was transferred to a volumetric flask and diluted to 500 ml. Portions of the solution were analysed for chloride by the Vohlhard method. The chloride arose from two sources: first, cyanogen chloride that had not been completely removed by the freezing-out treatment, and second, from the hydrogen chloride added to the system. Since it was not possible to estimate the amount of the latter present, the calculations were made on the basis that all the chloride arose from cyanogen chloride. The amount of carbon dioxide produced was then calculated by difference.

The excess of unreacted cyanogen chloride in the reaction vessel, *F*, was allowed to escape. There remained a white residue that could be divided into two portions, one soluble in chloroform and the other in water. After several extractions with chloroform the remaining residue was dissolved in water. This solution gave good qualitative tests for NH_4^+ and Cl^- ions. A Kjeldahl analysis on a dry portion of this residue gave a result in close agreement with that expected from ammonium chloride. Hence it was concluded that ammonium chloride was also a product of the hydrolysis reaction.

The results of a number of typical experiments are given in Table I. The weight of water present was calculated from the known volume of standard hydrochloric acid that was added. The amounts of ammonium chloride and carbon dioxide to be expected if all the water reacted according to the equation $CNCl + 2H_2O \rightarrow CO_2 + NH_4Cl$ are contrasted with the amounts of these substances actually produced in each experiment. In every case the amount of product found was less than that theoretically expected, but the differences are believed to be within the limits of experimental error of the method. These results indicate that the reaction between cyanogen chloride and water in the presence of hydrogen chloride is satisfactorily represented by Equation (1).

TABLE I

HYDROLYSIS EXPERIMENTS AT 20° C.

(Weights are in grams)

Expt.	Reactants		Products			
	$CNCl$	H_2O	NH_4Cl (calc.)	NH_4Cl (obs.)	CO_2 (calc.)	CO_2 (obs.)
4	6.34	0.3862	0.574	0.537	0.482	0.447
7	6.34	0.3838	0.570	0.534	0.469	0.461
8	6.34	0.3838	0.570	0.523	0.469	0.439
9	6.34	0.3838	0.570	0.533	0.469	0.436

As previously mentioned, the pressure increased to a maximum in all experiments, at which time the initial experiments were discontinued. On further investigation it was found that after the maximum pressure had been reached, there followed a decrease in pressure with time. Consequently, some experiments were allowed to proceed until no further pressure change occurred (approximately 21 days at 20° C.). The results of typical experiments are shown in Fig. 2. Experiment 9, at 20° C., was in progress for 20.3 days and the final steady pressure was 114.7 cm. of mercury. If the hydrogen chloride was not used up in the reaction, its partial pressure at the end of the reaction could be calculated. The pressure of carbon dioxide produced could also be calculated from the known amount of water added and the known

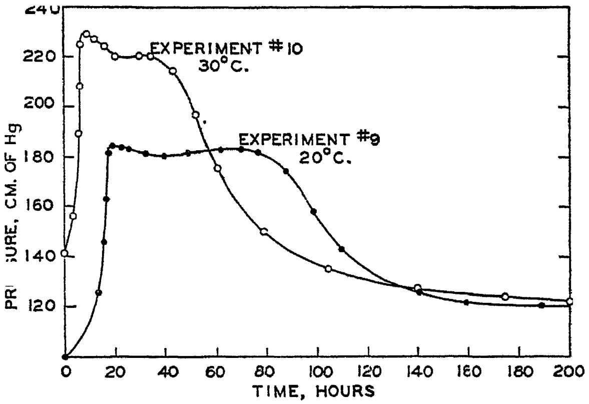

FIG. 2. *Pressure vs. time curves for the hydrogen chloride catalyzed hydrolysis and polymerization of cyanogen chloride at 20° and 30° C.*

volume of the apparatus. If, at the end of the reaction each of these substances was exerting its own partial pressure, and there were no other substances present with appreciable vapour pressures, the final pressure to be expected in the above experiment was calculated to be 117 cm. of mercury, which is in good agreement with the figure 114.7 cm. obtained.

When these experiments were terminated, all the liquid cyanogen chloride appeared to be gone but, in addition to the ammonium chloride formed, there was a considerable amount of a yellow-white crystalline solid. This substance was soluble in chloroform and was believed to be polymerized cyanogen chloride (i.e., cyanuric chloride). The chloroform solution of the polymer was allowed to evaporate to dryness and the amount of the polymer determined by weighing. The results for the amounts of ammonium chloride, carbon dioxide, and cyanuric chloride produced in several experiments are given in Table II. In Experiments 7 to 10, inclusive, a hydrochloric acid solution containing 0.0958 gm. of hydrogen chloride and 0.3838 gm. of water was added to 6.34 gm. of cyanogen chloride, giving a total weight of reactants of 6.718 gm. It will be observed from this table that a fairly satisfactory balance of materials was obtained.

TABLE II

HYDROLYSIS AND POLYMERIZATION PRODUCTS AT 20° C.

(Weights are given in grams)

	NH_4Cl	CO_2	$(CNCl)_3$	Total	Loss
Calc. from Equation (1)	0.570	0.469	5.679	6.718	—
Observed in Expt. 7	0.534	0.461	5.253	6.248	0.470
8	0.523	0.434	5.297	6.254	0.464
9	0.533	0.436	5.561	6.530	0.188
10[1]	0.541	0.466	5.666	6.673	0.045

[1] *Experiment 10 was carried out at 30° C. and the results are shown in Fig. 2 for comparison with Experiment 9. The shapes of the two curves are similar, but the maximum pressure was reached in 6.6 hr. at 30° C., whereas about 18 hr. were required at 20° C. Thus, the rate of this phase of the reaction was increased somewhat more than two and a half times for a 10 degree rise in temperature.*

An examination of the pressure vs. time curves (Fig. 2) indicates that the rate at which the pressure increases in the initial stages increases with time as if there were an autocatalytic effect. An experiment was carried out to ascertain whether solid ammonium chloride would act as an autocatalyst. This experiment was in all respects similar to Experiment 10 (Table II) except that 0.555 gm. of solid ammonium chloride was added to the reaction vessel before the reactants were admitted. However, the time for the maximum pressure to be reached was 6.6 hr., the same as in Experiment 10, thus indicating that the presence of solid ammonium chloride has little or no effect on the rate of the hydrolysis reaction.

A number of experiments were performed to study the effect of varying amounts of hydrogen chloride on the acid catalyzed hydrolysis of cyanogen chloride. The procedure in each case was the same; 10.25 gm. of cyanogen chloride were transferred to the reaction vessel and a known volume of standard acid added. The amount of hydrogen chloride in each experiment was controlled by the concentration of the solution used. The time for the completion of the hydrolysis reaction was taken as the time at which the first maximum in the pressure vs. time curve was reached. Fig. 3 is a graph of the weight per cent of hydrogen chloride used vs. the time of complete reaction of the water at 30° C. These results show that the reaction is rather slow at 30° C. if the percentage of hydrogen chloride is less than 1, but the rate increases very rapidly as the hydrogen chloride concentration is increased above 1.5%. However, even traces of hydrogen chloride in cyanogen chloride could result in dangerous pressure increases over a period of time if there was any appreciable amount of water present. An experiment was started in which only pure cyanogen chloride and water were present. An extremely slow pressure increase occurred over a period of four weeks. Whether this was due to a direct reaction between cyanogen chloride and water or whether it was due to catalysis by traces of acid, it is not possible to say.

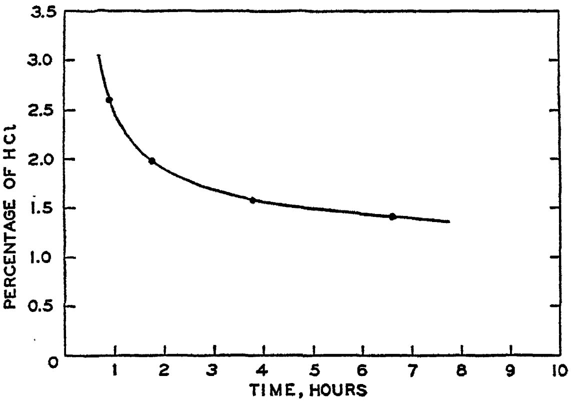

FIG. 3. *Weight per cent of hydrogen chloride vs. the time for complete reaction of water with cyanogen chloride at 30° C.*

2. *Polymerization Experiments*

A series of experiments were performed to study the effect of adding dry hydrogen chloride to cyanogen chloride at 30° C. Known amounts of pure cyanogen chloride and hydrogen chloride (generated by the action of sulphuric acid on sodium chloride and dried by passage through phosphorus pentoxide) were introduced into reaction vessels similar to those used in the study of the acid catalyzed hydrolysis. The progress of the reaction was followed by noting the pressure changes.

The pressure vs. time curves of a series of polymerization experiments are shown in Fig. 4, together with that for a blank (i.e., no hydrogen chloride present). In all such blank experiments there was no change in the vapour pressure of cyanogen chloride nor did any solid polymer separate out. One of these experiments extended over a period of six weeks, indicating that pure, dry cyanogen chloride is reasonably stable at 30° C.

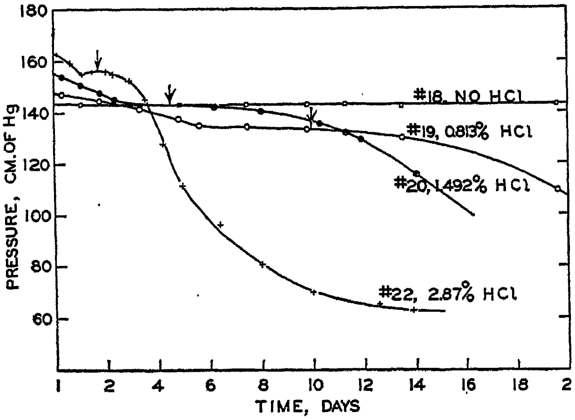

FIG. 4. *Pressure vs. time curves for the polymerization of cyanogen chloride with varying weight percentages of dry hydrogen chloride at 30° C.*

When the reaction vessels, to which hydrogen chloride had been added, were opened, they were found to contain a white crystalline solid and a small amount of a yellow liquid along with the hydrogen chloride that had been added. The greater the amount of hydrogen chloride that had been added, the shorter was the time required for polymerization of a given amount of cyanogen chloride. In the reactions involving larger amounts of hydrogen chloride, more of the yellow liquid was formed. It was also noticed that, in experiments in which polymerization had taken place slowly (smaller quantities of hydrogen chloride), fewer but larger crystals resulted. In one experiment a large crystal, approximately 1 by $\frac{3}{4}$ in., was formed. All the cyanogen chloride had apparently been used up by the time the tests were terminated because it could not be detected by its odour or its lachrymating effect. The odour of the products was similar to that which accompanies crude acetamide. Some of the larger crystals of polymer were washed with chloroform, dried, and found to melt at 142.5° C. This is 2.5 degrees lower than that reported by Whitmore (5) for cyanuric chloride. It was noted that the solid tended to sublime at temperatures in the vicinity of the melting point.

In the experiments shown in Fig. 4, the vapour pressure of each of the cyanogen chloride – hydrogen chloride mixtures was greater than the vapour pressure of pure cyanogen chloride, but the increase in pressure was approximately half as much as would be expected if the hydrogen chloride was insoluble in cyanogen chloride. This indicates that the solubility of hydrogen chloride in cyanogen chloride is appreciable.

The time for complete polymerization of the liquid phase was taken as the time that the pressure began to decrease from a fairly constant value (shown by arrows in Fig. 4), the decrease being due to polymerization of cyanogen chloride remaining in the gas phase (see discussion). The fact that crystals of the polymer formed on parts of the apparatus not in contact with liquid cyanogen chloride indicates that polymerization takes place directly from the vapour phase. Fig. 5 is a plot of the time required for complete liquid phase polymerization of a given quantity of cyanogen chloride vs. the percentage of hydrogen chloride. Although a direct relation between the concentration of hydrogen chloride and the rate of polymerization does not appear to exist, it is evident that the rate does increase rapidly as the concentration of hydrogen chloride is increased above 1%.

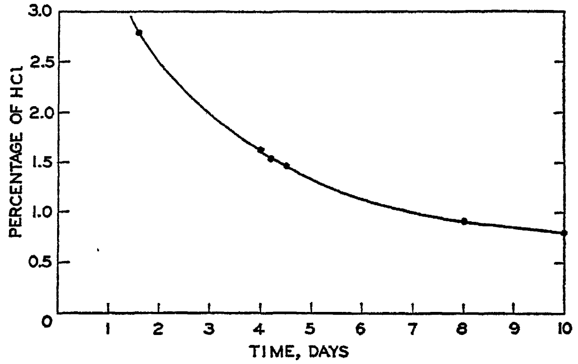

FIG. 5. *Weight percentage of hydrogen chloride vs. the time required for complete liquid phase polymerization of a given quantity of cyanogen chloride at 30° C.*

3. *Solubility Experiments*

A series of experiments were carried out to determine the extent to which carbon dioxide dissolves in liquid cyanogen chloride. The object of this part of the work was to obtain data that could be used to determine the correct pressure increase in the hydrolysis experiments. An apparatus was designed and constructed to measure the quantity of gas required to saturate a quantity of initially gas-free solvent. Unfortunately, the results obtained were not sufficiently reproducible to warrant publication. In an attempt to check the method and apparatus, experiments on the solubility of carbon dioxide in water were done, but the same inconsistencies appeared. The main difficulty was that the solubility, expressed as volume of gas dissolved per unit volume of solvent at 20° C., fell off rapidly for gas pressures less than 30 cm. of mercury. For gas pressures of about 50 cm. of mercury, results in reasonable agreement with those cited in the literature (3) were obtained, but the reproducibility was not good. The same type of difficulty was encountered in experiments on the solubility of carbon dioxide in cyanogen chloride. It can be stated, however, that at gas pressures above 30 cm. of mercury, the solubility of carbon dioxide in liquid cyanogen chloride is of the order of 8 ml. per ml. of solvent at 20° C.

Discussion

The reaction of cyanogen chloride with water in the presence of hydrogen chloride has been shown to proceed quantitatively according to the equation:

$$CNCl + 2H_2O \rightarrow CO_2 + NH_4Cl.$$

The reaction probably takes place in several steps, the hydrogen chloride acting as a catalytic agent in one or more of these steps. The reaction has been shown to be extremely slow in the absence of hydrogen chloride.*

The pressure vs. time curves for the hydrogen chloride catalyzed polymerization (Fig. 4) all have the same general shape, and the following is a suggested explanation. When the reaction is first initiated the total pressure is that due to the vapours of the pure cyanogen chloride – hydrogen chloride solution. As polymerization takes place the vapour pressure of the cyanogen chloride is reduced because the polymer formed is soluble in cyanogen chloride to some extent. This explains the first gradual decrease of total pressure with time. A point will be reached, however, where the cyanogen chloride becomes saturated with polymer and further polymerization leads to a separation of solid cyanuric chloride. Under these conditions the vapour pressure of a simple solvent would assume a fixed value which would persist until all the liquid had polymerized. However, this case is complicated by the presence of dissolved hydrogen chloride, and, as polymerization of the cyanogen chloride proceeds, some of the hydrogen chloride will be forced out of solution and may cause the pressure to rise again as in Experiment 22, Fig. 4. In some cases this effect was more gradual and did not result in a second maximum in the pressure vs. time curve. When all the liquid cyanogen chloride has polymerized, the total pressure begins to decrease slowly to its final value as the remaining cyanogen chloride vapour itself polymerizes.

The graphs of Fig. 2 show the characteristic double maxima that usually occur in the pressure vs. time curves for the acid catalyzed hydrolysis. The initial increase in pressure, to the first maximum, is due to the formation of carbon dioxide. Polymerization of cyanogen chloride probably takes place simultaneously with the hydrolysis. When the water has completely reacted, polymerization of the remaining cyanogen chloride continues until it is all transformed. Thus the explanation of the general form of the curves (Fig. 2), after the first maximum is reached, is similar to that suggested above with reference to Fig. 4, provided that the cyanogen chloride is not yet saturated with polymer. The only essential difference is that carbon dioxide and ammonium chloride are present along with hydrogen chloride, cyanogen chloride, and cyanuric chloride. The presence of carbon dioxide will affect the polymerization curve by a displacement along the pressure axis and may also contribute to the occurrence of the second maximum as it is forced out of solution by a decrease in the amount of solvent. When all the cyanogen chloride has polymerized the pressure has decreased to a value that was found to be the sum of the partial pressures of the carbon dioxide and hydrogen chloride.

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* *Additional experiments on the kinetics of this reaction in dioxane solution are now in progress in this laboratory.*

An examination of the results indicates that the rates of polymerization with and without the presence of water were quite different, the rate being considerably greater in the experiments in which water was initially present. For example, in Experiment 10 (Table II and Fig. 2) the time for complete liquid phase polymerization was about 31 hr. after the initiation of the reaction. In this case, 6.335 gm. of cyanogen chloride and 0.0958 gm. of hydrogen chloride were used, i.e., the mixture was 1.44% hydrogen chloride if the reaction is considered only from the standpoint of cyanogen chloride and hydrogen chloride. Referring to the graph in Fig. 5, the time required for the polymerization of 10.25 gm. of cyanogen chloride containing 1.44% of dry hydrogen chloride was 109 hr. In the hydrolysis experiment (Experiment 10), 0.640 gm. of cyanogen chloride reacted with water, leaving 5.695 gm. available for polymerization. If this amount had polymerized at the same rate as it does in the presence of dry hydrogen chloride, 60.5 hr. would have elapsed before complete liquid phase polymerization. Actually, however, this stage was reached in only 31 hr., making it very evident that the rates under the different conditions are not at all comparable. A possible explanation for this is that the amount of hydrogen chloride in actual contact with the cyanogen chloride may be greater in the hydrolysis experiments, as all the acid originally added mixed with the cyanogen chloride, whereas, in the polymerization experiments, the hydrogen chloride was added as a gas which did not all dissolve in the cyanogen chloride.

With the experimental method used it is not possible to calculate rate constants for the hydrolysis reaction, as an interpretation of the pressure increase is complicated by factors such as the solubility of carbon dioxide in the cyanogen chloride and by the polymerization of cyanogen chloride.

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THE ADSORPTION OF ALIPHATIC ACIDS ON ACTIVATED CHARCOALS[1]

By R. U. Lemieux[2] and J. L. Morrison[3]

Abstract

The adsorptions of acetic, propionic, butyric, and valeric acids from aqueous solutions on a series of coconut charcoals of different degrees of activation were determined. For purposes of interpretation the numbers of millimoles adsorbed per gram of charcoal were compared for pairs of acids. Unimolecular adsorption of the acids is indicated. Surface areas of the charcoal series were estimated. They range from 130 to 625 sq. m. per gm. of charcoal, depending on the adsorbate used and the degree of activation of the charcoal. Some insight into the activation process is given.

Introduction

Some knowledge of the internal structure of activated charcoal can be obtained by measurements of the surface area at different degrees of activation.

Many attempts have been made to measure the surface area of charcoal by adsorption from solutions. Generally these have consisted in determining the adsorption isotherm for a solute in a suitable solvent. By extending the concentration range until the amount of solute adsorbed per gram of charcoal appears to be independent of concentration, it is assumed that saturation of the charcoal–liquid interface by the solute is reached. If the size and orientation of the adsorbed molecules and the thickness of the adsorbed layer are known, the specific surface area of the adsorbent can be calculated.

This paper presents some experimental results which indicate that the adsorption of aliphatic acids (acetic to valeric) at the charcoal–water interface is unimolecular, and that activated coconut charcoal has multi-sized pores with a pore size distribution dependent on the degree of activation.

The adsorption of the lower normal aliphatic acids from aqueous solutions on various types of charcoal have been determined many times. For instance, Linner and Gortner (5) determined the adsorption of several organic acids on Norit charcoal. What is unique in the results that follow is that the charcoals employed were a series consisting of the same charcoal at different stages of activation.

Experimental

The coconut shell charcoal samples were obtained from the Standard Chemical Co. Ltd., Montreal. They consisted of a series of eight samples removed from the steam activator at approximate intervals of 24 hr. The eighth sample was nearly completely activated. Further steam treatment of the charcoal beyond Charcoal 8 causes a decrease in activity. This was shown experimentally in this laboratory for a similar charcoal series. In

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[1] *Manuscript received January 29, 1947.*
Contribution from the Department of Chemistry, University of Alberta, Edmonton, Alta.

[2] *Graduate student.*

[3] *Assistant Professor of Chemistry.*

Table I are given some data on these samples. The volume activities and mercury densities were determined by Dr. J. C. Arnell of Ottawa. The nitrogen adsorption measurements were made by M. Nay (7) using the method of Brunauer, Emmett, and Teller (2).

TABLE I

DATA ON THE COCONUT CHARCOALS

Sample No.	Volume activity[1]	Mercury density,[2] gm./cc.	Nitrogen adsorbed,[3] v_m millimoles/gm.
1	1.5	1.140	4.88
2	3.8	1.103	5.92
3	6.2	1.086	8.42
4	11.4	1.036	9 79
5	11 6	1.034	10.18
6	17.3	0.969	11.06
7	21.7	0.933	12.58
8	24.6	0.896	—

[1] *Volume activity—an empirical test based on carbon tetrachloride retentivity.*

[2] *Mercury density—charcoal density in mercury at ⅛ atm. pressure (3, p. 112).*

[3] *Nitrogen adsorption, v_m, is the volume of adsorbate that covers the surface with a monolayer.*

The acetic, propionic, butyric, and valeric acids were chemically pure grade, from Eastman Kodak Company. In some cases they were refractionated and the constant boiling fractions used. The sodium hydroxide solutions were free from carbon dioxide and standardized with potassium acid phthalate.

A weighed sample of charcoal (0.25 to 2.0 gm., corrected for moisture content) was placed in a 250 ml. Erlenmeyer flask. Acid solution (100 ml.) was accurately pipetted into the flask. To attain equilibrium, the flask was shaken for one-half hour and then allowed to stand for various lengths of time depending on the adsorbate.

A portion (25 ml.) of the equilibrium mixture was titrated with standardized sodium hydroxide solution, using phenolphthalein indicator. In this way the equilibrium concentration and the amount of acid adsorbed per gram were determined. Some experiments were made in a bath thermostatically controlled at 25.0 ± 0.1° C., and some at room temperature (23° to 27° C., summer 1943). No difference in the amount of saturation adsorption was found. Consequently room temperature was used in these experiments.

The effect of evacuation of the charcoal, both before and after contact with the solution, was tested. These tests gave the same results as the experiments without evacuation.

Results

The acids used in these experiments exhibited the typical Langmuir curve when the amount adsorbed per gram was plotted against the concentration in the substrate. The maximum amounts of the various acids adsorbed on charcoals of different degrees of activation are given in Table II. Maximum adsorption occurs at about 2.0 *N* for acetic, 0.5 *N* for propionic, 0.35 *N* for butyric, and 0.25 *N* for valeric acid.

The experimental results were interpreted by comparing the maximum adsorptions of the various acids with one another. This is done in Figs. 1, 2, and 3. Here the number of millimoles per gram (x/m) for each acid are plotted against the x/m of another particular acid, for each charcoal.

TABLE II

MAXIMUM MILLIMOLES OF ACID ADSORBED PER GRAM OF CHARCOAL

Charcoal No.	Acetic	Propionic	Butyric	Valeric
1	2.15	1.63	1.24	0.88
2	2.55	2.04	1.66	1.31
3	2.85	2.47	2.06	1.75
4	3.22	2.91	2.63	2.40
5	3.25	2.93	2.74	2.41
6	3.70	3.46	3.43	3.18
7	4.00	3.75	3.84	3.66
8	Insufficient charcoal	3.96	4.25	4.01

Some time studies were also made. The times required to reach equilibrium at saturation concentrations were measured by D. M. Miller (6) for Charcoal 3 (low activation) and Charcoal 7 (high activation). They are given in Table III.

TABLE III

EQUILIBRIUM TIMES OF ADSORPTION FROM SOLUTION ON CHARCOALS

Adsorbate	Initial concentration, M	Time, hr.	
		Charcoal 3	Charcoal 7
Acetic acid	2.3	16	4
Propionic	0.53	16	4
Butyric	0.37	10	6
Valeric	0.24	8	10
Caproic	0.039	4	16

Discussion

Surface Area

The adsorption measurements give consistent correlations with the volume activities, mercury densities, and nitrogen adsorptions.

In general, the charcoal density determined with mercury is very low compared with the absolute density of charcoal. Mercury does not penetrate the small pores of the charcoal. Therefore mercury density is an inverted measure of the pore volume. The acid adsorption increases as the mercury density decreases. Probably the processes of increase in pore volume and of increase in surface area occur simultaneously.

The charcoal surface areas presented to various acids have been calculated on the assumption of a unimolecular adsorption layer and vertical orientation of the adsorbate molecules. These are given in Table IV. In these calculations, an adsorbate area of 24.3Å^2 per molecule was used, as this area was found for some of these acids at the water–air and water–benzene interfaces (8, p. 50). In addition the surface areas presented to nitrogen have been calculated on the assumption of solid packing of the nitrogen molecules.

TABLE IV

SURFACE AREAS AVAILABLE TO ACID ADSORBATES

Sample	Area, sq. m. per gm.				
	Acetic	Propionic	Butyric	Valeric	Nitrogen[1]
1	316	240	182	128	408
2	375	300	244	193	495
3	419	363	303	258	704
4	474	428	387	353	819
5	478	431	403	354	852
6	544	509	505	468	924
7	589	551	565	538	1052
8	—	583	625	590	—

[1] *Calculated from v_m on the basis of a nitrogen molecular area of 13.8Å^2 (solid packing).*

The areas found with the acids were from about 130 to 625 sq. m. per gm., depending largely on activation and to a lesser degree on the size of the adsorbate molecule. A comparison of these areas with those obtained with nitrogen seems to indicate that the acids adsorb on only part of the charcoal surface. A comparison with the areas obtained by Fineman, Guest, and McIntosh (3) with nitrogen on a different charcoal series indicates that the two series of charcoal are similar.

Unimolecular Adsorption

Figs. 1, 2, and 3 are plotted on the basis of Table II. For comparison the straight line cutting the origin at 45° is added to each figure. This line represents the amount of acid adsorbed when plotted against itself—that is, against the same number of molecules adsorbed on the same surfaces. It will be noted that all pairs approach the slope of unity, particularly in the region of low activation. The intercept on the abscissa indicates the extra number of millimoles of the smaller molecule adsorbed. This extra number is approximately the same for consecutive pairs of acids. The validity of the extrapolations in Figs. 1, 2, and 3 may be questionable. However, the authors have no reason, either from experimental results or from logic, to doubt that such extrapolations are valid.

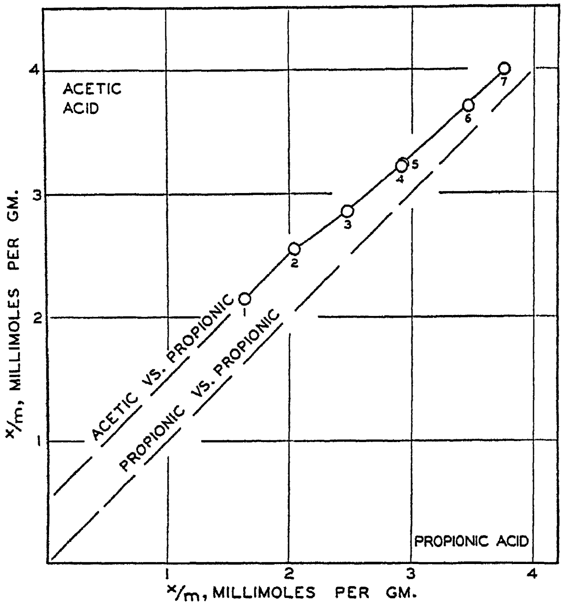

FIG. 1. *Comparison of acetic with propionic acid for charcoal series.*

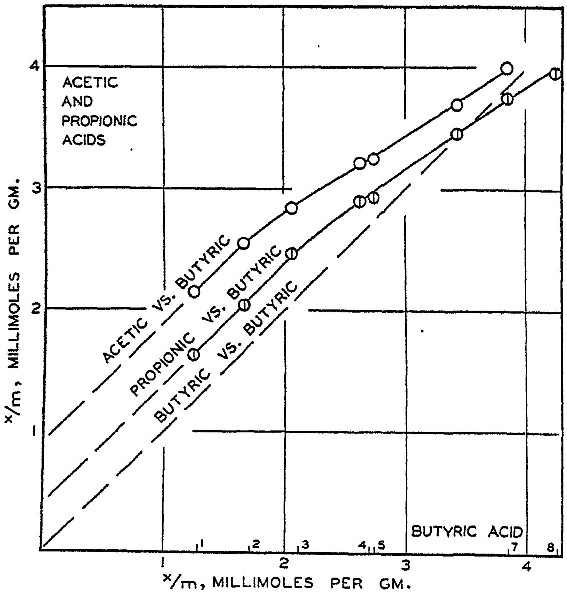

FIG. 2. *Comparison of acetic and propionic with butyric acid for charcoal series.*

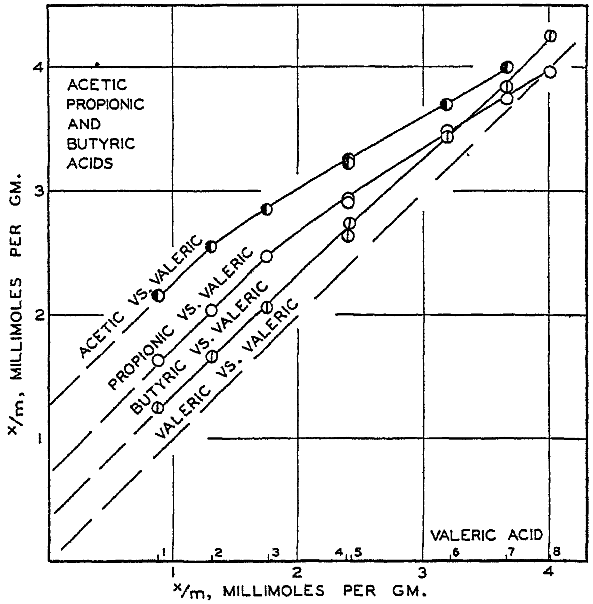

FIG. 3. *Comparison of acetic, propionic, and butyric with valeric acid for charcoal series.*

The intercepts may be interpreted as a measure of the extra relative area of the pore walls available to the smaller molecules. The fact that the lines are at a 45° angle at lower activations is interpreted as indicating unimolecular adsorption.

An alternative explanation is possible, based on the assumption that the same area is available to all the molecules. One might then suggest further that the acid molecules lie flat on the charcoal surface, covering areas proportional to their lengths. However, this conception is contradictory to two general facts. First, coconut charcoal usually presents different surface areas to different adsorbates (1), and second, the aliphatic acids tend to orientate vertically at saturated water–air interfaces (4, p. 1886).

Pore Size and Size Distribution

Assuming that charcoal is a complex network of pores of various diameters, and that the aliphatic acids adsorb unimolecularly from solution at the water–charcoal interface, it is possible to estimate the average thickness of the pore walls. For Charcoal 3 this is about 3 carbon atoms, a thickness of about 4.5Å. Probably many walls are thicker, and many thinner than this.

An estimate of the average pore diameters will be made in a later paper. However, some idea of pore size distribution may be gained by examining Figs. 1, 2, and 3. The adsorbed films are in dynamic equilibrium with the outside solution. Therefore, though the adsorbate molecules may have a common cross-sectional area, they present to the pore openings an average size which depends largely on their length. Acetic acid will reach pore walls that valeric cannot. This is supported by the fact that the intercepts in the figures are in the consistent direction. The further fact that these intercepts are approximately proportional to the increase in chain lengths of the adsorbate molecules indicates an even distribution of the pore sizes for the less activated Charcoals 1 to 3. However, the nitrogen areas of the charcoals indicate that there are a large number of very small pores not reached by these acids.

Thus, it is quite possible to account for the results on the basis of unimolecular adsorption and, particularly for the less activated charcoals, of an even distribution of pore sizes. This distribution refers to sizes of the same order of magnitude as the sizes of the adsorbate molecules.

Orientation of the Adsorbate Molecules

It has been assumed that the molecular orientation is vertical in the saturated acid films at the water–carbon interface. The results provide some evidence for the validity of this assumption.

While the less activated Charcoals 1, 2, and 3 show distinct and parallel differences in the number of moles of acid adsorbed, the more activated Charcoals 6, 7, and 8 tend towards identity in the number of moles of acids adsorbed. Changes in porosity, in which the dimensions of the pores are similar to the dimensions of the acid adsorbates, account for the behaviour of the less activated charcoals. Eventually, however, the activation process must give rise to sufficiently large pores to permit all acids to enter most of the internal surface. This is the probable explanation for the fact that the four acids from acetic to valeric give about the same number of moles adsorbed for Charcoals 7 and 8. Differences in the packing of the adsorbed molecules may account for the fact that Charcoals 7 and 8 adsorb more butyric acid than propionic acid. Similarly Charcoal 8 adsorbs more valeric acid than propionic acid.

A larger proportion of pores accessible to all these acid molecules would be expected as activation proceeds. This expectation, together with the fact that the number of moles adsorbed approaches identity at higher activations, suggests a similar area being occupied by each molecule (of the acid series). This indicates vertical orientation, the common cross-section being either the methyl or carboxyl groups. The latter, being the larger, is considered the determining one. Presumably in a saturated film, the acid molecules are oriented perpendicularly to the carbon surface, with the hydrocarbon end towards the carbon and the carboxyl end towards the solution.

Since the amount adsorbed per gram of charcoal can be determined with an accuracy of 1% or better, the accuracy of the determination of the surface areas of charcoal by this method is limited by the accuracy to which the area covered by each molecule is known, and, of course, by the accessibility of these adsorbates to the internal surface.

It is well to remember that, when pore radii and adsorbate molecules are similar in size, the meaning of *area* as measured by these adsorbates is somewhat uncertain. This point will be considered in a later paper.

Activation

The activation process for coconut shell charcoal can be elucidated somewhat by an examination of the results and calculations.

The process appears to involve an increase in the total pore volume. At the same time, for charcoals up to No. 3, the pore size distribution is fairly constant and regular for pore sizes of the same order as the sizes of the molecules of the acids used.

However, as activation proceeds beyond the stage of that of Charcoal 3, this constant progressive development deteriorates. The rate of increase of the number of pores accessible to molecules of the size of those of acetic and propionic acids decreases compared with that of the number of the size accessible to butyric. This is shown by the fact that the curves for acetic and propionic acids plotted against valeric, Fig. 3, take a downward trend while that for butyric remains parallel. It would appear that pores of the size accessible to butyric and valeric acid molecules are forming at the expense of pores of the size accessible to molecules of propionic and acetic acids. This process continues until the stages of activation of Charcoals 7 and 8 are reached. In Charcoal 6, for instance, all pores accessible to propionic are accessible to butyric, but not yet to valeric. Acetic acid, with the smallest molecule, has in all these charcoals access to some pores that are inaccessible to the other acids.

An increase in the average pore radius with increased activation is implied in this paper. This is corroborated by McIntosh and his collaborators (3, p. 117) who found an increase in pore size with activation for a similar charcoal series. In their case, they calculated the pore radii from water vapour adsorption data by the Cohan equation.

The maximum of the activation process would probably occur when further treatment (steam activation) would decrease the surface area, that is, when a net gain in surface area no longer would obtain by sacrificing small pores for large ones. That this is so was shown for samples of another coconut shell charcoal, prolonged activation of which resulted in a decrease in the amount of acid adsorbed from solution.

Further confirmation of the ideas presented in this paper with respect to porosity changes during the activation process is given by the fact that the times to reach equilibrium for Charcoals 3 and 7 (Table III) are inverted for the acid series. Whereas in the less activated charcoal the longer chain acids reach equilibrium sooner, in the more activated charcoal the shorter chain acids do so. For the charcoal with smaller pores (Charcoal 3) the time for penetration of the solution is the slow process. Therefore the longer chain acids reach their limiting porosity sooner. For the charcoal with larger pores (Charcoal 7), in which all the acids penetrate to about the same internal area, the rate of diffusion of the acid molecules from the external solution to the adsorbed layer is the slow process. Therefore the shorter chain acids reach equilibrium sooner.

Acknowledgment

The authors express their appreciation to Dr. O. Maass and Dr. R. McIntosh for their interest and assistance in this work.

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PHOTOMETRIC MICRODETERMINATION OF CALCIUM[1]

By H. A. DeLuca[2]

Abstract

A method is described for the photometric determination of amounts of calcium ranging from 0.04 to 0.16 mgm. The calcium is precipitated as the oxalate. The latter is converted to the carbonate by heating at 475° to 500° C. for one hour. The carbonate is dissolved in 1 ml. of 0.01 *N* hydrochloric acid. The excess acid is allowed to liberate iodine by reacting with potassium iodate and potassium iodide. The absorption of the iodine solution is measured by use of an Evelyn colorimeter, and the calcium originally present in the sample is determined from calibration data.

Introduction

During the course of an investigation involving the estimation of the inorganic constituents of animal tissues, it became necessary to determine small amounts of calcium. The colorimetric method presented here was developed for this purpose.

Sobel and Kaye (5) have described a procedure for the determination of calcium based upon the following reactions.

$$Ca^{++} + C_2O_4^{--} \rightarrow CaC_2O_4 \qquad (1)$$

$$CaC_2O_4 \rightarrow CaCO_3 + CO \qquad (2)$$

$$CaCO_3 + HCl\ (\text{excess}) \rightarrow CaCl_2 + H_2O + CO_2 \qquad (3)$$

$$6HCl + KIO_3 + 5KI \rightarrow 3I_2 + 3H_2O + 6KCl \qquad (4)$$

The calcium is precipitated as the oxalate (Equation 1). The calcium oxalate is converted into the carbonate by heating (Equation 2). A known amount of hydrochloric acid is added to the calcium carbonate (Equation 3). The acid remaining after the carbonate has been neutralized is allowed to liberate iodine (Equation 4). The amount of iodine thus produced is maximal in the absence of calcium in the sample and decreases as the calcium content becomes greater. In the method of Sobel and Kaye this iodine is determined by titration with sodium thiosulphate whereas in the present method the photoelectric colorimeter is utilized for this purpose.

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Contribution from the Department of Biochemistry, Faculty of Medicine, University of Western Ontario, London, Ont. Supported in part by a grant-in-aid from the National Research Council of Canada.

[2] *Assistant Professor of Biochemistry.*

Method

Reagents

Hydrochloric acid, approximately 0.01 N

Hydrochloric acid, approximately 2 N

Bromphenol blue, 0.04%, prepared according to the method of Clark (1)

Ammonium oxalate, saturated solution

Ammonium oxalate, 0.5% solution

Ammonium hydroxide, approximately 1 N, prepared by diluting 7 ml. of concentrated ammonium hydroxide to 100 ml.

Potassium iodate, 0.5% solution

Potassium iodide, 10% solution

Potassium iodide, 10% solution in 0.002 N sodium hydroxide; 10 gm. of potassium iodide and 10 ml. of a stock solution of 0.02 N sodium hydroxide are made up to 100 ml.

Calcium solution, 2.00 mgm. of calcium per ml., prepared by dissolving 0.500 gm. of chemically pure calcium carbonate in sufficient 2 N hydrochloric acid and diluting with distilled water to 100 ml. Before the final adjustment of volume is made, 1 ml. of concentrated hydrochloric acid is added in order to prevent the growth of moulds.

Procedure

Between 0.04 and 0.16 mgm. of calcium contained in 5 ml. of solution is measured into a selected Pyrex centrifuge tube (see Discussion). One drop of bromphenol blue, sufficient 2 N hydrochloric acid to change the colour of the indicator to its acid colour, and 0.2 ml. of saturated ammonium oxalate are added in the order given. The pH is adjusted to approximately 3.5 (a faint blue colour of the indicator) by adding 1 N ammonium hydroxide drop by drop.

The tube is allowed to stand for one to two hours with occasional shaking and is then centrifuged for 15 min. at 3000 r.p.m. The supernatant liquid is decanted and the tube inverted on a blotter or towel for 10 min. The mouth of the tube is wiped dry with a small piece of filter paper. The precipitate is then suspended in 0.3 ml. of 0.5% ammonium oxalate and the tube is again centrifuged for 15 min. As before, the supernatant liquid is removed by decantation and the tube inverted for a 10 min. period.

The centrifuge tube is then placed in a cold muffle furnace. The temperature is gradually raised to 475° to 500° C. and held there for at least an hour. The tube is then allowed to cool to room temperature after which exactly 1 ml. of 0.01 N hydrochloric acid is added. Solution of the calcium carbonate is facilitated by means of a stirring rod, which is left in the tube during subsequent operations. Heating the tube in a water-bath (85° to 95° C.) for 15 min. with occasional stirring completes solution and expels the carbon dioxide.

The tube is then stoppered with a one-hole rubber stopper, through which the stirring rod is allowed to pass. After cooling for 30 min. to room temperature, 0.2 ml. of 0.5% potassium iodate and 0.2 ml. of 10% potassium iodide are added in that order. The tube is allowed to stand for 15 min. to ensure complete liberation of the iodine, at the end of which time 10 ml. of the alkaline 10% potassium iodide is pipetted into the tube. The contents is then rinsed into a 25 ml. volumetric flask and made up to volume.

Prior to the reading of the solutions in the colorimeter (420 mμ), the latter is adjusted by the following procedure. To 1 ml. of distilled water contained in a centrifuge tube are added 0.2 ml. of 0.5% potassium iodate and 0.2 ml. of 10% potassium iodide. The tube is allowed to stand for 15 min., at the end of which time 10 ml. of the alkaline 10% potassium iodide is added. The contents of the tube is diluted to 25 ml. as before. Two such tubes are prepared and the colorimeter is adjusted to the average of the so-called 'centre-settings'. (The centre-setting is given by the reading of the galvanometer following the removal of the tube as prepared above from the colorimeter, the latter having previously been set to read 100 with this tube in place). The iodine solutions obtained from the samples are now read in the colorimeter and their calcium content is determined from calibration data.

Calibration Curve

Samples containing known amounts of calcium ranging from 0.04 to 0.16 mgm. per 5 ml. in steps of 0.01 mgm. were prepared from the stock solution. For the purpose of ascertaining what precision could be expected from the method, four samples of each concentration were treated according to the procedure given above. The results are given in Table I and are shown

TABLE I

CALIBRATION DATA

(1) Calcium, mgm.	(2) Galvanometer readings	(3) Slope of curve, mgm. per division	Mean deviation		Range of values Max. → Min.	
			(4) Of galvanometer readings	(5) Of calcium, as %	(6) Of galvanometer readings	(7) Of calcium, as %
0.00	17.9	—	±0.0	—	—	—
0.04	24.0	0.0067	±0.1	±1.7	0.2	3.4
0.05	26.2	0.0045	±0.1	±0.9	0.4	3.6
0.06	27.4	0.0040	±0.4	±2.7	0.9	6.0
0.07	31.4	0.0036	±0.2	±1.0	0.6	3.1
0.08	33.8	0.0031	±0.3	±1.2	1.1	4.3
0.09	37.0	0.0025	±0.8	±2.2	2.0	5.6
0.10	40.8	0.0024	±0.7	±1.7	1.8	4.3
0.11	45.8	0.0022	±0.3	±0.6	0.9	1.8
0.12	51.9	0.0019	±0.5	±0.8	1.4	2.2
0.13	55.2	0.0017	±0.4	±0.5	1.2	1.6
0.14	62.4	0.0015	±1.1	±1.2	3.6	3.9
0.15	70.8	0.0013	±1.3	±1.1	3.1	2.7
0.16	78.5	0.0010	±0.5	±0.3	1.0	0.6

graphically in Fig. 1. The mean value and deviation for the galvanometer readings are shown in Columns 2 and 4, respectively. By using the slope of the curve at each point (Column 3), the mean deviation of the galvanometer readings has been calculated as a percentage of the amount of calcium present (Column 5). In Column 6 is given the difference between the minimum and maximum values of the galvanometer readings for the four samples at each concentration. In Column 7 this difference is expressed as a percentage of the calcium present.

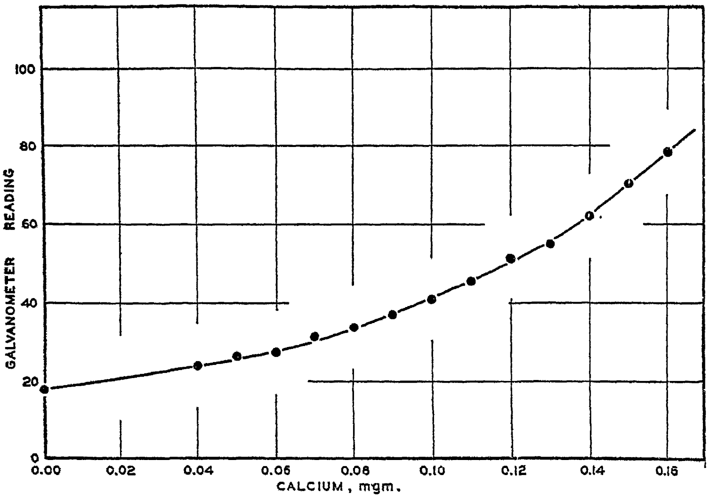

Fig. 1

Sixty-two determinations were performed during the course of the calibration. The results from six of these were discarded, as the deviations from the mean in these instances were of a magnitude suggestive of manipulative error.

Discussion

The Pyrex centrifuge tubes used for the determinations were selected with some care. Only those with the most constricted tips were chosen, as such tubes appeared to hold the precipitate more firmly during decantation of the supernatant liquid.

The use of 5-ml. samples for the calcium precipitation was adopted for several reasons. Some of the tissue solutions to be analysed were so dilute that a smaller volume did not contain an amount of calcium sufficient for analysis by the colorimetric method. On the other hand, more concentrated solutions could be analysed by selecting a suitable volume and diluting it to 5 ml. with distilled water prior to the precipitation of the calcium. The use of a larger volume has the additional advantages that it simplifies the adjustment of the pH to a given value, and that during decantation there is a more complete recovery of the supernatant liquid, which is desirable when further analysis is contemplated.

A somewhat lower temperature for the conversion of calcium oxalate to the carbonate has been employed inasmuch as heating at 560° C. for one hour, as recommended by Sobel and Kaye, resulted in samples that had almost no ability to neutralize the acid solution. Siwe (4) has indicated that unless special tubes are used, the calcium precipitate may attack the glass at temperatures of 550° to 600° C. Data obtained by Willard and Boldyreff (6) show that the oxalate–carbonate conversion proceeds to completion in one hour at a temperature of 450° C.

The potassium iodide solution decomposes with time to yield free iodine. Decomposition proceeded slowly in the stock solution contained in a brown glass bottle, but the same solution decomposed more rapidly after transference to a smaller clear glass container. The potassium iodate solution appeared quite stable. Sobel and Kaye (5) give a simple procedure for testing both reagents at once, namely, the mixing of equal volumes of the iodide and iodate solutions followed by the addition of a few drops of a starch solution. Actually, a small amount of free iodine should be of no consequence in a colorimetric method inasmuch as the use of a blank corrects for this. Notwithstanding, fresh solutions were prepared whenever decomposition of the iodide had occurred.

The alkaline 10% potassium iodide solution is used for a twofold purpose. First, it prevents the evaporation of the iodine liberated, and second, it acts to intensify the colour of the latter. Both of these effects are produced by the formation of the compound KI_3, as pointed out by Sendroy and Alving (3). Decomposition of the potassium iodide is overcome by the use of the sodium hydroxide, as suggested by Flox, Pitesky, and Alving (2). This is especially desirable at this point of the procedure owing to the fact that such a large volume (10 cc.) of the iodide solution is necessary to achieve the purposes indicated above. However, experiment indicates that this solution should not be much more alkaline in the sodium hydroxide than 0.002 *N*. Solutions of higher concentration (0.01 *N*) caused a disappearance of a detectable amount of the iodine liberated in the course of the calcium analysis, probably as a result of the reaction given below.

$$2NaOH + I_2 \rightarrow NaI + NaIO + H_2O$$

The exact normality of the 0.01 *N* hydrochloric acid need not be known. It is advisable to prepare a reasonably large volume of this acid at one time in order to avoid the necessity of recalibrating the colorimeter with each fresh batch of this reagent. Hydrochloric acid of this concentration was found to be quite stable. The iodine liberated by 1 ml. of acid (which is the equivalent of an analysed sample containing no calcium) as measured in the colorimeter may be used to indicate any change in the strength of the acid. In measuring the latter, the same pipette was used throughout the calibration and subsequent analyses.

Several departures from the customary use of the Evelyn colorimeter were made. A single colorimeter tube was used in obtaining the calibration curve and in all analyses. After reading a solution in the colorimeter, the contents was poured from the tube, and the tube allowed to drain for a few seconds. The tube was then rinsed with several 3 ml. portions of the solution about to be measured. Inasmuch as this avoids the differences in colorimeter tubes, it is thought justifiable to report the galvanometer readings to the nearest 1/10 division rather than to the nearest $\frac{1}{4}$ division, as suggested in the directions accompanying the instrument.

A consideration of the results obtained for the calibration curve indicates what precision may be expected in the analysis of samples of unknown calcium content. For the lowest amount of calcium (0.04 mgm.) the galvanometer readings for the four samples (23.8, 24.0, 24.0, 24.0) show smaller differences, but the percentage error is relatively large. A glance at Table I shows that at this point a difference of 0.1 division in two galvanometer readings produces a deviation of nearly 2%. For samples containing larger amounts of calcium (0.15 mgm.), the galvanometer readings (69.2, 69.8, 72.0, 72.3) show much larger differences, but these cause relatively smaller percentage deviations.

The method as described above cannot be used for samples containing more than 0.16 mgm. calcium. However, it could be extended readily to higher values simply by employing greater volumes or stronger solutions of the reagents indicated.

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COAGULATION AND SURFACE LOSSES IN DISPERSE SYSTEMS IN STILL AND TURBULENT AIR[1]

By G. O. Langstroth[2] and T. Gillespie[3]

Abstract

Smoke chamber studies have been made of the ageing of ammonium chloride smokes under various controlled degrees of turbulent air motion as well as in still air. The changes in mass concentration and particle number were followed for 5.5 hr. under each set of conditions, and some data on particle size distribution were obtained. The logarithm of the mass concentration was found to vary linearly with time under all conditions. None of the particle number data lent themselves to interpretation on the basis adopted by previous workers. They were described quantitatively by equations developed from general postulates which take into account loss to various surfaces. The equations permitted analytical separation of coagulation and surface effects, and the constant descriptive of the latter was closely related to that associated with mass loss. The coagulation constant for still air was found to be only slightly greater than the ideal Smoluchowski value. A description was obtained of the manner in which the various constants increased with the degree of air motion.

The ageing of aerosols in still air has been studied extensively (for general discussions, see references 13 and 14).* It has been found (6, 9, 10, 14*) that the increase in particulate volume ($1/n$) with time (t) may be represented by

$$1/n = 1/n_0 + Kt, \tag{1}$$

where n denotes the number of particles per cubic centimetre at time t, and n_0 that at an early arbitrary time origin. Data given in the literature do not extend beyond ageing times of about 100 min. but it has been stated (9) that the linear relation holds for intervals as long as 250 min. It has been customary to interpret K as the coagulation constant. The values determined for it have been considerably greater than that for an ideal aerosol as calculated from a modification of Smoluchowski's theory of coagulating sols (2, 8, 9, 14).

The ageing of aerosols in turbulent air has received comparatively little attention. The results of studies that have been made (4, 11) do not lend themselves readily to interpretation in terms of fundamental processes because of the difficulty of translating the Tyndall beam brightness data obtained to terms of particle number and size. Except in specially designed laboratory experiments, however, problems involving turbulent air conditions are most often encountered.

In the attempt to obtain a better understanding of the factors involved in the general ageing process, studies have been made of ammonium chloride smokes under various controlled degrees of turbulent air motion ranging from the static condition upward. The changes in the mass of dispersed material and number of particles per cubic centimetre (mass concentration and particle

[1] *Manuscript received March 6, 1947.*
Contribution from the Department of Physics, University of Alberta, Edmonton, Alta.

[2] *Professor of Physics.*

[3] *Instructor in Physics.*

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* *And "Disperse systems in gases", in Trans. Faraday Soc., Vol. 32, pp. 1042-1300. 1936.*

number) were followed for 330 min. under each set of conditions. None of the data for these long periods, including data for still air, could be interpreted on the basis that coagulation was the sole factor responsible for the reduction in particle number. They are described, however, by equations developed from general postulates. The equations permit an analytical separation of effects produced by coagulation and by loss to adjacent surfaces, and are consistent with fact in the various points for which a comparison has been possible. Changes in the degree of air motion alter the values of constants in the equations so that the effect on the processes involved may be described with the aid of determined curves for the constants. In particular, the relation between particulate volume and time differs in form from that given in Equation (1).

1. Apparatus, Techniques, and Experimental Procedure

(a) *The Smoke Chamber and Stirring Mechanism*

The smoke chamber was a 1.12 m. cube having its internal walls finished with acid-proof paint. The stirrer used to produce air motion consisted of two 60.5 by 32.5 cm.^{2} coplanar cardboard vanes mounted at the ends of a 60.5 by 91.5 cm.^{2} light wooden frame so that a gap of 26.5 cm. was left between them. Each vane was pierced by a series of 15 equally spaced 5 by 5 cm.^{2} holes. The stirrer was supported on a horizontal axle parallel to the length of the vanes and passing down the middle of the central gap. It was oscillated through an angle of 180° from the vertical at any selected frequency by a motor driven system of gears and shafts external to the chamber. The frequency was determined with the aid of a revolution counter incorporated in the driving system. This device was used in preference to ordinary fans because of its periodic reversal of motion, the ease of control and adjustment, and its well defined characteristics as a stirrer.

(b) *Specification of the Degree of Air Motion*

The average amount of air passing through a given small volume per unit time regardless of direction was taken as an index of the degree of air motion. The characteristics of the air motion with different stirring rates were investigated with the aid of an instrument of the heated thermocouple type developed for the purpose. The head of the device consisted of six thermocouple junctions with heating coils, arranged in the form of a child's jack and extending about 1.5 cm. in each dimension. The readings were independent of the direction of air flow, and the time lag was not excessive (equilibrium was attained within one minute on an abrupt change from 12 to 46 m. per min. steady air velocity). The instrument was calibrated under conditions of uniform air flow. Readings of the effective air speed for different stirring rates were made at 16 systematically distributed points throughout the chamber in a series of preliminary experiments. They were found to be closely proportional to the oscillation frequency of the stirrer. Furthermore, they were remarkably similar at different points, excepting those close within the corners of the chamber. For example, with a frequency of 30 min.$^{-1}$, they varied only from 34 m. per min. for points directly off the high velocity outer edge of the stirrer to 29 m. per min. for points near the wall at the axle; with the device mounted on the stirrer the reading was 40 m. per min., but it decreased to 17 m. per min. close within the corners. In presenting the results on smoke a value V (m. per min.) has been assigned to each experiment as an index of the degree of air motion. This value is the space-average air speed (as found in preliminary experiments) corresponding to the stirrer oscillation frequency used.

(*c*) *Production of the Aerosol*

The smoke generator consisted of a centrifugal blower whose output passed through a control valve into a 7 cm. diameter metal pipe leading into the chamber. The pipe contained a Pitot tube to permit adjustment of the air flow to a standard value, and a nichrome heating coil placed near the exit end. A standard amount (87 mgm.) of ammonium chloride placed in a Pyrex boat on the coil was decomposed in two minutes with a heating current of 8.0 amp. A small fan within the chamber provided rapid cooling and dilution of the products as they emerged from the exit end of the pipe. The generator was designed with the aim of obtaining a series of aerosols of similar characteristics, for it is known (10, 14) that reproducibility is favoured with 'blown' smokes. In our experiments the mass concentration at three minutes after completion of smoke production varied from about 40 to about 60 mgm. per m.^{3} and the corresponding particle number from about 2×10^5 to about 4×10^5 cc.$^{-1}$ (Table III).

(*d*) *Determination of Mass Concentration*

Samples were obtained by electrical precipitation using a modified form of the tube (diameter 1.2 cm., length 6.5 cm.) described by Drinker and Hatch (3). The central electrode was enclosed in Pyrex to permit thorough cleaning and to avoid contamination. In sampling, 500 cc. of the aerosol was first drawn through the precipitator with no applied voltage by lowering the water level in an attached system. A further volume of 250 to 4000 cc. (depending on conditions) was then drawn through with an applied voltage of 10 kv., which produced a discernible glow between the electrodes. The deposit was dissolved in 50 cc. of distilled water, and the resulting solution was analysed with Nessler's reagent. Precipitates ranged from 0.040 to 0.002 mgm. of ammonium chloride. Tests carried out with two precipitator tubes in series indicated that precipitation was complete for aerosols both in the early and late stages of life. The initial flushing procedure, which was required to obtain a sample representative of the aerosol in the chamber, did not result in a detectable deposit in the precipitator tube.

(*e*) *Determination of Particle Number*

A thermal precipitator (7)* mounted on a 2.5 cm. diameter brass tube extending 10 cm. into the chamber was used in the determination of the number of particles per cubic centimetre. In taking a sample, 500 cc. of the aerosol was first drawn through the brass tube from an exit at the precipitator end, and 5 cc. was drawn through the cold precipitator by lowering the water level in an attached small-bore graduated tube. A current of 1.25 amp. was then passed through the precipitator wire (No. 32 B & S nichrome) and a volume of 0.5 to 10 cc. (depending on conditions) was drawn through, starting 5 to 10 sec. after the current had been turned on. The flow rate of 2 to 4 cc. per min. was well below the value of 6.5 cc. per min. suggested (7) as an upper limit for efficient deposition, and the deposits formed on the polished glass disks had straight, sharp, leading edges—a characteristic indicative of complete precipitation (7). The deposit formed during the initial flushing procedure was found to be negligible. It was necessary to stop the stirring mechanism during sampling: the stoppage period was not more than one minute for each sample.

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* *See also "Disperse systems in gases", in Trans. Faraday Soc., Vol. 32, pp. 1042-1300, 1936.*

The deposits on the disks were 9 mm. long and less than 1 mm. wide. They were examined under a magnification of 440 × using dark field illumination produced by a narrow light beam approximately normal to the optic axis of the microscope. The number of particles in each of 10 equally spaced crosswise strips of width 2.3×10^{-3} cm. was counted for each deposit with the aid of a mechanical stage and a Whipple disk in the eyepiece. The known ratio of the examined to the total area of the deposits permitted calculation of the total number of particles deposited, and the number of particles per cubic centimetre was found from this value and the known volume of the sample. The fact that samples taken with no smoke in the chamber gave inappreciable counts ruled out dust as a complicating factor in these experiments.

In some of the earlier experiments, aerosol samples were diluted with air before precipitation in order to reduce the particle number and thus facilitate counting. The validity of the procedure was established by comparing the results for a series of direct and diluted samples taken alternately. Dilution was abandoned on arranging to draw samples of 0.5 to 1.0 cc. with an accuracy of 3%.

(f) *Particle Size Estimation*

Four subsidiary experiments, two with still air and two with a high degree of air motion ($V = 50$ m. per min.) were performed to provide information on particle size distribution. Thermal precipitator samples were taken every 30 min. for a period of 280 min. The deposits were examined with substage illumination and a magnification of 950 ×. The particles in crosswise strips selected as for particle number counts were classified into size groups by comparing them with the smallest square in the Whipple disk (projected area $2.2 \times 2.2\ \mu$). Since this procedure is based on the appearance in two dimensions it may be subject to systematic error. The size groups adopted were: less than 0.3, 0.3 – 0.6, 0.6 – 0.9, 0.9 – 1.1, 1.1 – 1.4, 1.4 – 1.7, and 1.7 – 2.2 μ in apparent radius. In the results shown in Fig. 3, the number in each size group expressed as a percentage of the total has been plotted at the median radius for the group, that for the first being plotted at 0.2 μ.

(g) *The Procedure in Ageing Studies*

The generation of smoke was complete within a two minute period but the fan in the chamber was operated for three minutes longer. It was then turned off and the stirrer set in oscillation and maintained at the selected oscillation frequency. All subsequent times were reckoned from a zero set at the moment of turning off the fan. Particle number and mass concentration samples were taken at intervals of 30 min. for a period of 5.5 hr. (see Tables I and I*A*). Counts were made for the former immediately, but analysis of the latter was permissible at any period within 24 hr. if the precipitation tubes were well stoppered. The total volume drawn from the chamber during an experiment in flushing and sampling did not exceed 1.7% of the chamber volume. A series of experiments was performed with various degrees of air motion (see Tables I and I*A*). After each the chamber was well aired and cleaned.

The deposit on the bottom of the chamber at the end of an experiment under still air conditions was visibly greater than the deposit on the top and side walls. With stirred air, the distribution of the deposit appeared similar although the stirrer acquired a deposit similar to that on the bottom of the chamber.

A series of experiments was performed to ascertain the extent to which particles deposited on the walls were swept off again by air motion. The procedure was identical with that already described, but all surfaces were coated heavily with oil. Since subsidiary tests showed that particles were wet immediately on striking an oiled surface, it seems reasonable to assume that return to the aerosol was eliminated in these experiments.

2. Experimental Data

Particulate volume ($1/n$) and mass concentration (m) data for a series of experiments (serial numbers *D*38, *D*40, etc.) are given respectively in Tables I and I*A*. The corresponding data obtained with oiled chamber walls are given in Tables II and II*A*. For reasons to appear later, values calculated from Equation (7) are included in Tables I and II. It appears desirable that the data be given in some detail since the interpretation differs fundamentally from that given previously by various workers for data covering a more restricted range.

TABLE I

PARTICULATE VOLUME VS. TIME DATA (DRY CHAMBER WALLS)

The tabulated values are $10^6/n$ cc.*

t, min.	V = 0 m./min.				V = 1.1 m./min.		V = 5.4 m./min.	
	*D*38		*D*40		*D*75		*D*74	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
0	5.2	5.6	4.8	5.2	—	—	—	—
2	—	—	—	—	—	—	—	—
5	—	—	—	—	2.7	3.6	2.1	2.9
30	6.8	6.8	7.1	6.6	4.3	4.7	3.6	4.0
60	8.3	8.2	7.6	7.9	6.7	6.0	5.8	5.8
90	10.4	9.5	9.5	9.5	8.6	7.6	7.3	7.7
120	—	—	11.4	11.2	9.7	9.4	10.1	10.0
150	—	—	—	—	10.7	11.3	11.8	12.9
180	14.0	14.6	15.2	15.1	11.9	13.8	15.7	16.1
210	15.8	16.7	17.4	17.7	15.5	17.2	21	20
240	19	19	21	20	19	19	25	25
270	22	21	24	23	20	23	29	30
300	24	24	28	26	28	27	36	36
330	26	27	29	30	32	31	43	44

t, min.	V = 11 m./min.				V = 22 m./min.		V = 29 m./min.			
	*D*76		*D*77		*D*73		*D*56		*D*58	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
0	—	—	—	—	—	—	—	—	—	—
2	—	—	—	—	—	—	4.8	4.5	—	—
5	3.5	3.5	4.3	4.4	4.3	4.8	—	—	3.1	3.3
30	4.9	4.8	6.3	5.8	6.0	6.3	5.4	6.2	5.4	4.7
60	6.5	6.6	8.2	8.6	9.5	8.8	10.8	8.5	7.5	7.7
90	8.6	8.9	9.0	9.8	12.1	11.4	13.2	11.2	8.4	9.1
120	11.2	11.5	11.1	12.3	14.3	14.8	—	—	12.7	12.3
150	14.6	15.0	14.0	15.2	19	19	17.4	18.2	16.0	15.8
180	22	19	20	19	26	24	24	23	21	20
210	25	24	22	23	31	29	29	29	27	26
240	30	30	27	28	35	36	35	35	31	33
270	33	37	34	34	41	44	47	44	45	41
300	46	46	43	42	59	54	54	54	52	52
320	57	53	—	—	—	—	—	—	—	—
325	—	—	—	—	—	—	—	—	61	62
330	—	—	54	50	67	66	62	66	—	—

Values under the heading 'Calc' were calculated from Equation (7) with the constants as given in Table III.

PARTICULATE VOLUME VS. TIME DATA (DRY CHAMBER WALLS)—*Continued*
The tabulated values are $10^6/n$ cc.*—*Continued*

t, min.	*V* = 35 m./min.				*V* = 40 m./min.				*V* = 50 m./min			
	*D*62		*D*63		*D*54		*D*55		*D*51		*D*60	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
0	—	—	—	—	—	—	—	—	—	—	—	—
2	—	—	—	—	7.3	5.8	5.6	4.8	4.4	4.0	—	—
5	3.3	3.3	—	—	—	—	—	—	—	—	—	—
30	5.4	5.0	6.0	6.5	—	—	9.0	7.3	6.5	7.0	6.0	7.2
60	6.8	7.5	9.9	9.5	8.2	11.4	8.5	11.0	12.9	11.5	12.8	11.5
90	12.6	11.0	15.9	13.5	16.7	16.3	12.8	15.8	16.3	17.4	23	18
120	15.2	15.0	—	—	22	22	26	22	28	25	26	25
150	19	20	23	24	28	29	30	30	38	36	29	35
180	27	27	32	31	54	39	43	40	53	50	43	49
210	34	36	43	41	53	51	55	53	73	70	69	69
240	46	48	52	52	64	67	68	70	98	96	97	95
270	65	63	61	67	88	89	92	93	128	129	—	—
300	82	82	79	85	115	113	125	123	176	176	164	176
320	—	—	—	—	—	—	—	—	—	—	—	—
325	—	—	—	—	—	—	—	—	—	—	250	233
330	109	107	118	109	145	145	147	159	232	239	—	—

**Values under the heading 'Calc.' were calculated from Equation (7) with the constants as given in Table III.*

TABLE IA

MASS CONCENTRATION (MGM. PER $M.^3$) VS. TIME DATA FOR THE EXPERIMENTS OF TABLE I

t, min.	*V* = 0		1.1	5.4	11		22
	*D*38	*D*40	*D*75	*D*74	*D*76	*D*77	*D*73
10	38	46	44	40	44	44	44
40	38	44	38	33	33	—	33
70	32	38	35	26	23	25	25
100	26	34	27	20	19	20	17
130	24	37	30	18	15	15	12.5
160	20	32	18	15	14	13	12.0
190	18	25	17	12.5	10	10	8.0
220	23	20	14	10	6.7	7	5.2
250	19	25	13	10	5	6.7	6.0
280	17	21	13	8	4	5	3.3
310	14.6	20	—	—	—	—	—

t, min.	*V* = 29		35		40		50	
	*D*56	*D*58	*D*62	*D*63	*D*54	*D*55	*D*51	*D*60
10	42	52	40	48	47	53	43	44
40	33	40	33	37	37	40	27	23
70	30	35	25	27	22	23	23	20
100	20	25	16	14	16	15	12	12
130	14	22	12	11	12	12	6	11
160	18	18	10.6	10.5	12	10	8	6.5
190	12	13	8	9	7.5	7	4	5.3
220	8.7	6.5	5.5	5.5	5	3	3	3
250	5	6.0	4	4	3.5	3.5	1.3	1.5
280	4	—	5	4	2.8	2.7	0.8	1.2
310	—	—	—	—	—	—	—	—

TABLE II

DATA CORRESPONDING TO TABLE I BUT FOR OILED CHAMBER WALLS

t, min.	$V = 0$		$V = 11$				$V = 40$	
	$W80$		$W78$		$W79$		$W81$	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
5	2.4	3.0	2.5	2.9	2.9	3.0	2.5	2.6
30	4.3	4.1	4.1	4.1	4.1	4.0	4.5	4.5
60	5.6	5.3	5.9	5.6	6.7	5.5	7.7	7.2
90	7.1	6.7	7.5	7.3	7.9	7.3	10.5	10.7
120	8.0	8.0	9.8	9.7	9.0	9.3	13.3	15.1
150	9.7	9.6	11.1	12.0	11.8	11.9	20	21
180	11.3	11.1	14.2	15.0	15.7	14.8	28	29
210	12.9	13.2	19	19	18.3	18.0	39	39
240	16.5	15.3	22	23	23	22	48	51
270	16.8	17.7	27	28	25	27	63	67
300	20	20	32	34	33	33	90	88
330	26	23	41	41	—	—	—	—

TABLE IIA

MASS CONCENTRATION (MGM. PER M.^{3}) VS. TIME DATA FOR THE EXPERIMENTS OF TABLE II

t, min.	$V = 0$	11		40
	$W80$	$W78$	$W79$	$W81$
10	40	44	44	42
40	34	30	31	23
70	28	28	28	15
100	27	22	23	14
130	24	18	19	10
160	25	16	18	9
190	21	13	15	6
220	18	10	11	3.3
250	18	9.0	10	2.5
280	17	8.0	9.0	—

Particulate volume vs. time plots in the manner of previous workers are shown in Fig. 1 for some of the data. They are not described by Equation (1). Even for still air the curve exhibits a concavity upward, although for a period of about 200 min. it is reasonably linear. The initial portion has a slope corresponding to a K value of 5.1×10^{-8} cc. per min. as defined by Equation (1), compared to values ranging from 3.0×10^{-8} to 7.9×10^{-8} cc. per min. obtained for ammonium chloride smoke by previous workers (6; 9; 10; 14, p. 46).

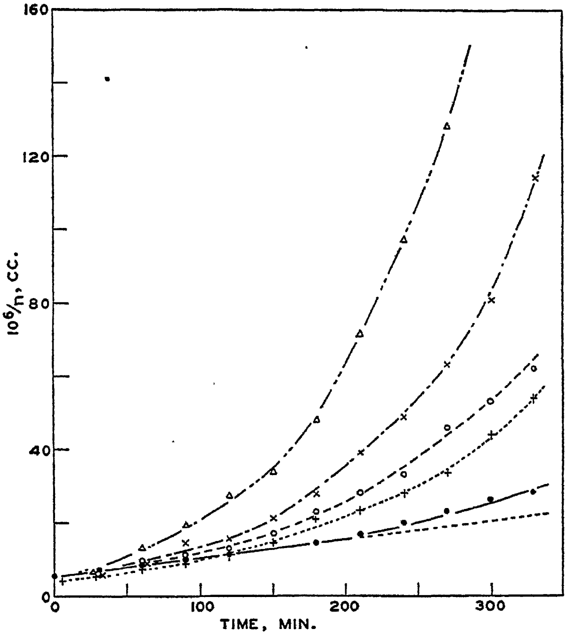

FIG. 1. *Particulate volume vs. time curves for various degrees of air motion. The symbols* ●, +, O, ×, *and* △ *are associated respectively with V values of 0, 11, 29, 35, and 50 m. per min. Each point is an average value for two experiments.*

Plots of log (m) vs. time as illustrated in Fig. 2 were found to be linear for all degrees of air motion over the investigated range. This relation has been reported previously (12) to hold for various types of fanned smokes. In addition, some still air data from the literature, when plotted similarly, provide further support. Not only are the plots linear but their slopes are strikingly similar. For example, the data for two zinc oxide smokes studied

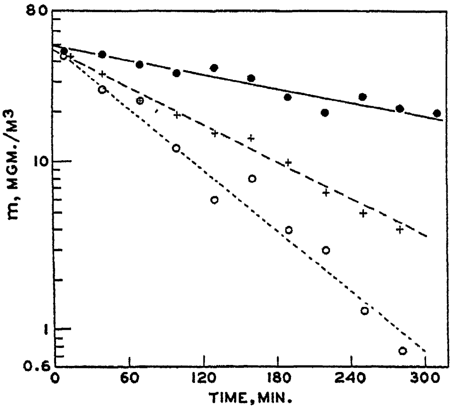

FIG. 2. *Mass concentration vs. time curves for various degrees of air motion. The symbols* ●, +, *and* O *are associated with V values of 0, 11, and 50 m. per min. The points represent single determinations.*

by Whytlaw-Gray and Speakman (15) yield a 'mass loss constant' (defined by Equation 3) of 3.6×10^{-3} min.$^{-1}$ on disregarding the first point in each which is stated to be erroneous, while some data for an ammonium chloride smoke (14, p. 19) give a value of 3.0×10^{-3} min.$^{-1}$. In comparison, our own data for still air yield values of from 3.2×10^{-3} to 3.6×10^{-3} min.$^{-1}$ (Table III).

The results of the particle size distribution experiments described in Section 1 (*f*) are given in Fig. 3.

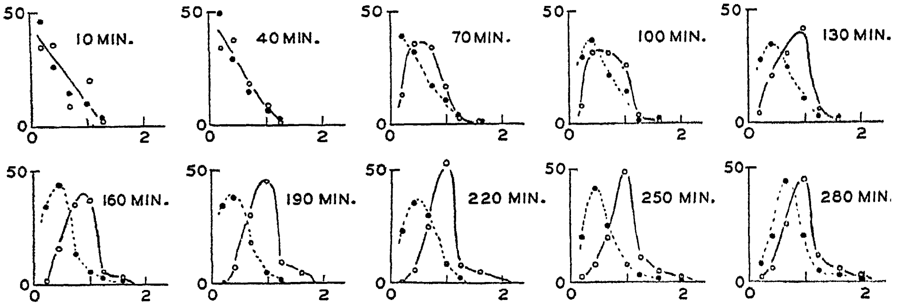

FIG. 3. *Estimated particle size distributions. The symbols* ○ *and* ● *are associated with V values of 0 and 50 m. per min. The ordinates refer to the frequency and the abscissae to the apparent radius in microns.*

3. Theoretical Aspects of the Ageing Process

The following considerations lead to a quantitative description of the experimental data.

In a turbulent medium, air is being brought constantly into contact with various surfaces, and since practically all particles striking a surface stick to it (Ref. 5, and the present data) there is a consequent decrease in mass concentration and particle number. The rate of decrease in the former quantity under a given set of conditions should be proportional to the mass concentration m, so that

$$dm/dt = -\alpha m, \tag{2}$$

where α denotes the 'mass loss constant'. It follows that

$$\ln(m) = \ln(m_0) - \alpha t \tag{3}$$

over periods for which α may be taken as independent of time, where m_0 denotes the mass concentration at $t = 0$. As previously stated, Equation (3) describes our data and receives strong support from other sources.

Other things being equal, the chance of a particle striking a surface should be proportional to the particle number n, so that the rate of decrease in particle number due to such loss is

$$(dn/dt)_l = -\beta n, \tag{4}$$

where β denotes the 'loss constant'. Since the chance of collision between two particles is proportional to n^2, the rate of decrease in particle number because of coagulation may be written,

$$(dn/dt)_c = - kn^2, \tag{5}$$

where k denotes the coagulation constant. It follows that the total rate of decrease in n is

$$dn/dt = - (kn^2 + \beta n) . \tag{6}$$

Both k and β may be expected to increase with increasing air motion because of the greater chance of particle collisions and of the increased rate at which air is brought into contact with surfaces. For aerosols confined in a chamber, β should depend on chamber geometry since a large ratio of wall surface to volume must favour rapid removal of particles. In addition, both k and β may be expected to depend to some extent on particle size, i.e., the greater mobility of small particles favours a high collision rate and the greater momentum of large particles a high loss rate on deflection of air currents at surfaces. Particle size is subject to change during the ageing of an aerosol, and strictly speaking k and β are functions of time.

For intervals over which time variations in k and β may be disregarded, it follows from Equation (6) that

$$\ln(1/n + k/\beta) = \ln(1/n_0 + k/\beta) + \beta t , \tag{7}$$

where n_0 denotes the particle number at $t = 0$. Furthermore,

$$n = n_0 \, e^{-\beta t}/\phi \tag{8}$$

$$(\Delta n)_l = \beta/k \, . \ln \phi , \tag{9}$$

where $\phi = 1 + n_0 k/\beta \, . \, (1 - e^{-\beta t})$ and $(\Delta n)_l$ denotes the reduction in particle number due to surface losses during the interval 0 to t. The corresponding expression for coagulation losses is readily found.

A close relation may be expected to exist between the loss constant β and the mass loss constant α. If the average mass of particles in the aerosol and of those lost to surfaces at a given time be denoted by μ and μ', respectively, one may write $m = \mu n$ and $dm/dt = \mu'(dn/dt)_l$. Hence in view of Equations (2) and (4),

$$\alpha/\beta = \mu'/\mu . \tag{10}$$

For an ideal homogeneous smoke α and β should be equal.

Previous workers have adopted Equation (1) of the introduction in the interpretation of ageing data for still air. This relation follows directly from integration of Equation (5) with K substituted for k, i.e., constancy of mass concentration is assumed. The mechanisms responsible for the observed decrease in mass concentration in still air may involve sedimentation, diffusion of particles to surfaces, and air currents set up by temperature gradients and disturbances caused in sampling. Whatever their nature it appears reasonable to assume that the rate of decrease in particle number and in mass concentration due to surface losses are proportional to n and m, respectively, as specified by Equations (4) and (2). On this basis Equations (2) to (10) should be applicable to still as well as to turbulent air conditions. This expectation is borne out by the experimental data.

It might be thought at first sight that the mechanisms of loss in still and turbulent air have little in common, since in general sedimentation velocity is negligibly small compared to the air velocity in turbulence. The former is, however, always superimposed on the latter, and the time average of the latter is zero. Consequently a tendency for material to be deposited most densely on the surface below the aerosol must be expected, and is found in experiments.

No applicable theory of sedimentation appears to have been worked out in detail. An idea of the importance of diffusion as a loss mechanism in still air is readily obtained from a consideration of the diffusion of homogeneous non-coagulating particles to the 'absorbing' walls of a spherical chamber of radius ρ_0 in the absence of gravity. Analogous equations in the theory of heat flow are well known (1). For a uniform initial distribution, the fraction F of the particles that remains after a time t is given by

$$F = \frac{6}{\pi^2} \sum_l \frac{1}{l^2} e^{-\frac{D\pi^2 l^2 t}{\rho_0^2}} , \tag{11}$$

where l takes on successive integer values, and the diffusion constant D for spherical particles of r microns radius is given (2, 14) by

$$D = 10^4 RT/6\pi N\eta r . \tag{12}$$

R, T, N, and η denote, respectively, the gas constant, the temperature, Avogadro's number, and the coefficient of viscosity of air. According to these equations the loss by diffusion in a five hour period is less than 5% for particles of 0.5 μ radius, and no greater than 10% for particles as small as 0.001 μ in radius. Loss by diffusion therefore seems likely to play only a minor role in the ageing process under laboratory conditions.

The value of the coagulation constant k at room temperature and atmospheric pressure for an ideal aerosol whose spherical particles of r microns radius coagulate on touching may be calculated from the well known expression based on Smoluchowski's theory of coagulating sols (2, 8, 9, 14), i.e.,

$$k = 1.77 \times 10^{-8} (1 + 0.089/r) \text{ cc. per min.} \tag{13}$$

The equation predicts a decrease in k of about 9% when the particle radius increases from 0.5 to 1.0 μ. This feature is of interest in connection with the neglect of the time dependence of k in the integration leading to Equation (7) (cf. Fig. 3).

4. Analysis of the Particle Number Data

Following the suggestion of Equation (7), it was found that plots of log $(10^6/n + E)$ vs. time became linear on selection of a suitable value for the constant E by trial. Examples are shown in Figs. 4 and 5. The linearity of the curve was a fair criterion of the suitability of E for data associated with large V values, but was less critical for plots of smaller slope. Under the worst conditions (still air data) a value of 6 or 7 produced linearity (Fig. 5), but higher values did not result in a noticeable concavity upward such as shown in Fig. 4. In these circumstances a value of E was selected to produce

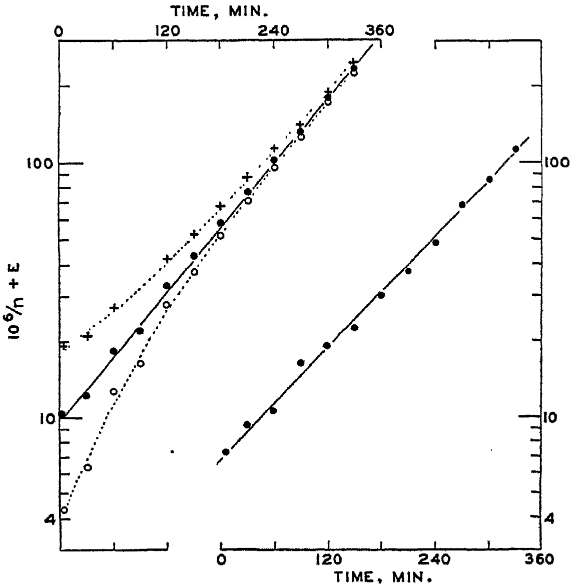

FIG. 4. *Data for single experiments plotted as suggested by Equation (7). The symbols* ○, ●, *and* + *in the plot at the left (abscissae values at the top) are associated with E values of 0, 6.0, and 15, and a V value of 50 m. per min. The plot at the right (abscissae values at the bottom) is associated with an E value of 4.0 and a V value of 35 m. per min.*

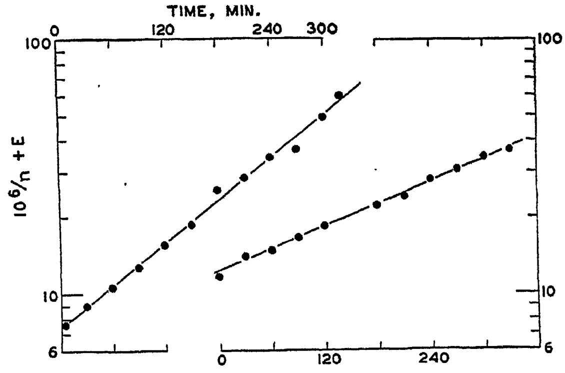

FIG. 5. *A companion graph to Fig. 4. The left and right hand plots are associated respectively with V values of 11 and 0 m. per min., and E values of 4.0 and 7.0.*

linearity and to be consistent with other features to appear later. The loss constant β was calculated from the slopes of the curves, and the coagulation constant k from the values of E and β (see Equation 7). The values of the constants for the entire data are given in Table III.

TABLE III

A SUMMARY OF THE EXPERIMENTAL VALUES OF THE CONSTANTS IN EQUATIONS (3) AND (7)

V, m./min.	Exp. No.	m_0, mgm./m^3	$n_0 \times 10^{-4}$, cc.$^{-1}$	$\alpha \times 10^3$, min.$^{-1}$	$\beta \times 10^3$, min.$^{-1}$	$k \times 10^8$, cc./min.	$k/\beta \times 10^6$	α/β
0.0	*D38*	39	18	3.2	3.0	2.1	7.0	1.1
0.0	*D40*	49	19	3.4	3.3	2.3	7.0	1.0_4
0.0	*W80*[1]	41	33	3.6	3.3	2.3	7.0	1.1
1.1	*D75*	47	29	5.2	4.4	2.2	5.0	1.2
5.4	*D74*	43	40	6.2	5.5	2.8	5.0	1.1
11	*D76*	45	31	8.3	6.4	2.6	4.0	1.3
11	*D77*	47	24	7.4	5.8	2.3	4.0	1.3
11	*W78*[1]	45	36	6.8	5.8	2.3	4.0	1.2
11	*W79*[1]	45	34	6.2	5.5	2.2	4.0	1.1
22	*D73*	48	23	9.0	6.2	3.1	5.0	1.4
29	*D56*	47	23	8.1	6.4	3.2	5.0	1.3
29	*D58*	60	32	8.5	6.9	2.8	4.0	1.2
35	*D62*	48	33	9.6	8.3	3.3	4.0	1.2
35	*D63*	48	24	9.6	7.6	3.8	5.0	1.3
40	*D54*	52	18	10.8	9.0	3.6	4.0	1.2
40	*D55*	56	22	11.0	8.7	4.3	5.0	1.3
40	*W81*[1]	40	42	10.8	8.5	4.3	5.0	1.3
50	*D51*	49	26	14.0	9.7	5.8	6.0	1.4
50	*D60*	47	25	12.8	9.9	4.9	5.0	1.3

m_0 and n_0 were obtained by extrapolation of the appropriate time curves.

[1] *Oiled chamber walls.*

5. Discussion

Plots such as Figs. 4 and 5 may give an erroneous impression of the experimental scatter, since a constant has been added to each $10^6/n$ value. For this reason particulate volumes as calculated from Equation (7) using the data of Table III have been included in Tables I and II for comparison with observation. The average deviation of calculated from observed values for the more than 200 determinations given was 6.2%. This is comparable to the scatter of determined points about linear $1/n$ vs. time curves obtained by previous workers for still air and ageing times of about 100 min. Published data (6, 9, 10) exhibit average deviations of about 5, 4, and 7%, and the overall frequency distribution of deviations is almost identical with our own. It is considered therefore that Equation (7) describes the entire particle number data as well as may be expected in view of the difficulty of attaining high precision in this type of aerosol work.

A comparison of the results obtained with dry and with oiled chamber walls shows no marked differences (Table III and Fig. 7). It is concluded that particles once deposited were not removed from the dry walls to any serious extent.

Application of Equation (7) to the data for still air yields a value of 2.2×10^{-8} cc. per min. for the constant k (Table III). The coagulation constant for an ideal aerosol as calculated from Equation (13) is 1.9×10^{-8} cc. per min. for particles of 1 μ radius and 2.1×10^{-8} cc. per min. for particles of 0.5 μ radius (cf. Fig. 3). As previously stated the value of K of Equation (1) obtained from the early portion of $1/n$ vs. time plots was 5.1×10^{-8} cc. per min., in agreement with the results of previous workers.

For a homogeneous aerosol the ratio α/β should be unity (Equation 10). For a non-homogeneous aerosol, loss of the heavier particles must be favoured—in sedimentation when the air is still, and in the deflection of air currents at surfaces when the air is in motion. Hence α/β should be greater than unity, but perhaps not very much so if the particle size range is small. Furthermore, both α and β should increase with the rate at which air is brought into contact with surfaces, and if the particle size distribution is not much altered (cf. Fig. 3), they should do so in roughly the same proportion. Both these features are characteristic of the data. It is shown in Fig. 6 that β is quite closely proportional to α regardless of the degree of air motion. It is shown in Table III that the ratio α/β is somewhat greater than unity. These facts provide strong support for the ideas advanced in Section 3, since β was determined analytically from particle number data and α directly from

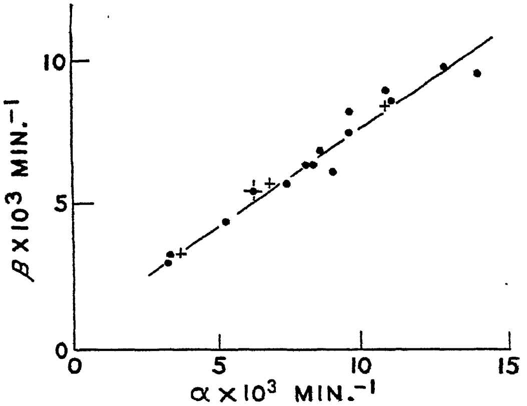

FIG. 6. *To illustrate the interdependence of α and β. The plot includes data for V values from 0 to 50 m. per min. The symbols + denote results obtained with oiled chamber walls.*

an entirely independent set of mass concentration data. The manner in which α, β, and k increase with the degree of air motion (index, V, m. per min.) is shown in Fig. 7.

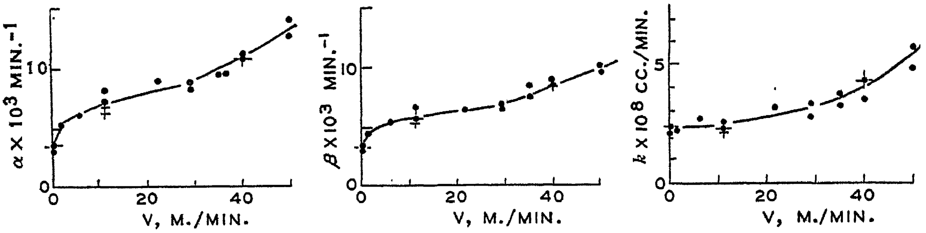

FIG. 7. *Changes in α, β, and k with increasing air motion. The symbols + denote results obtained with oiled chamber walls.*

In view of the wide range of conditions investigated, a purely fortuitous agreement between the equations and the data appears highly unlikely. The equations resulting from integration must be regarded, however, as descriptive of a special case, i.e., that for which time variations in α, β, and k may be disregarded. They would not be expected to apply, for example, to aerosols having a much smaller particle size.

It follows from the ideas expressed in Section 3 that the relative importance of coagulation and surface loss in the ageing process depends strongly on conditions. The importance of the former mechanism should be relatively great for dense aerosols since the rate of coagulation depends on n^2 while the rate of loss depends on n[*]. During the life of an aerosol the relative importance continually shifts to favour the latter mechanism. For the conditions of the experiments described, the rates of disappearance and the total numbers removed by each mechanism may be calculated separately for any given time with the aid of Equations (4), (5), (8), and (9) and the constants given in Table III.

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[*] *In general, previous investigators have worked with aerosols having an initial particle number several times that of our smokes.*

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AN ACETYL DERIVATIVE OF HEPARIN[1]

By H. J. Bell[2] and L. B. Jaques[3]

Abstract

An acetyl derivative of heparin corresponding to one mole of acetyl per four hexose units has been prepared by passing ketene through a suspension of heparin in acetone. The derivative possesses the same biological activity as the original heparin. It can be deacetylated in neutral solutions without loss of activity by raised temperatures, and like heparin, it is inactivated in acid solution.

Heparin is a polysaccharide possessing a very specific and very marked biological property, namely, its anticoagulant action on blood. Its clinical use has been hindered by the extreme rapidity with which it is excreted or destroyed by the body (Jaques (4)). We therefore thought it of interest to attempt to synthesize derivatives of this substance. However, while heparin is resistant to high temperatures at neutrality, it is very sensitive to acid and alkali (Charles and Scott (1)). Even brief exposure to relatively weak acid or alkali will completely destroy its anticoagulant activity. Hence the usual methods for preparing derivatives of carbohydrates are not suitable for the preparation of heparin derivatives. Hurd, Cantor, and Roe (3) have prepared acetyl derivatives of sugars by passing ketene through a suspension of the sugar in anhydrous acetone. We have applied this method to heparin and succeeded in preparing an acetyl derivative of heparin without any loss in anticoagulant potency.

Methods and Results

Acetyl determinations were made in the Kuhn–Roth apparatus, as described by Roth (9). The sample was hydrolysed by heating at 100° C. for 2½ hr. with 5% aqueous sodium hydroxide. After distillation, the acetic acid was titrated with 0.01 N sodium hydroxide. The blank on the reagents was 0.477 ml. of 0.01 N sodium hydroxide. The determination of acetyl in acetanilide gave 31.7% acetyl (theoretical, 31.8%).

Anticoagulant activity was determined by means of the Charles and Scott (5) modification of the Howell cat assay. In some cases the product was also checked by Miss A. G. Macdonald for its action on dog's blood *in vitro* and *in vivo*, as described by Jaques and Macdonald (6). The *heparin* used was the neutral sodium salt kindly supplied by the Connaught Medical Research

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[2] *Lecturer, Department of Physiology, University of Manitoba, Winnipeg, Man.; formerly Research Assistant, Department of Physiology, University of Toronto, Toronto, Ont.*

[3] *Professor of Physiology, University of Saskatchewan, Saskatoon, Sask.; formerly Assistant Professor, Department of Physiology, University of Toronto.*

Laboratories, University of Toronto, and had an assay value of 110 anticoagulant units per mgm. It contained 12.1% water, which was removed by drying over phosphorus pentoxide *in vacuo*. pH values were determined with the Beckman glass electrode.

Acetyl Content of Heparin

Since heparin contains glucosamine, Jorpes (7) assumed that it must contain acetyl. However, Charles and Todd (2) reported that they could not get consistent values for the acetyl content of heparin. Masamune, Suzuki, and Kondoh (8) explained this on the basis of a formation of acetic acid from glycuronic acid by sulphuric acid (10%) during the determination. More recently Wolfrom, Weisblat, Karabinos, McNeely, and McLean (10) have reinvestigated this question and failed to find any acetyl in purified heparin.

Determinations of acetyl were conducted on the sample of neutral sodium salt of heparin. These consistently gave a value of 1.13 to 1.20% acetyl, corresponding to an acetyl content of 0.37 mole. However, when the neutral sodium salt of heparin was dissolved in water (pH 6.94), the solution boiled for seven seconds, and then titrated, a titration value equivalent to 0.57% acetyl was obtained. Likewise, this amount of acid could be distilled from the aqueous neutral solution of sodium heparin. It is evident, therefore, that this value is not O- or N- acetyl. This fact was further demonstrated in control experiments on the acetylation procedure.

The neutral sodium salt of heparin was suspended in acetone at 55° C. for three hours. The 'acetyl' content remained at 1.13%. In a second control experiment, a large excess of heparin (0.66 gm.) was suspended in acetone and ketene was passed through for two hours. It had previously been found that no acetylation took place if an excess of heparin was present. The product now contained only 0.64% acetyl (0.2 mole). The latter value was therefore considered to be the 'acetyl' value of heparin itself.

Conducting the hydrolysis with *p*-toluenesulphonic acid instead of sodium hydroxide made no difference in the acetyl value.

As shown by Charles and Todd, the fundamental unit of heparin is a four-hexose unit containing two glucosamine, two glycuronic acid, and five sulphuric acid residues. As the degree of polymerization of this unit and the chain length are both unknown, we have reported our values in moles per four-hexose unit. An increase in the acetyl content of 3.19% is equivalent to the introduction of one mole of acetyl per four-hexose unit.

Preparation of the Acetyl Derivative

The heparin was dried to constant weight *in vacuo* over phosphorus pentoxide at room temperature, and an 88 mgm. sample was suspended in 25 ml. of acetone (freshly distilled from calcium chloride) in a 100 ml. flask. The flask, equipped with a reflux condenser, was placed in a water-bath at approximately 55° C. and ketene was passed in from a generator for one hour or more. The suspension was then centrifuged, the precipitate washed twice with 5 ml. of acetone, and dried *in vacuo* to give 90.6 mgm. of acetyl heparin. The average acetyl content of the compound was 4.02% and the anticoagulant potency 131 units per mgm.

When ketene was passed through samples for one, two, three, and eight hours, the acetyl content of the samples was 3.98, 4.06, 4.01, and 4.44%, and the biological activity was 130, 130, 131, and 132 units per mgm.

One sample treated with ketene for two hours when freshly prepared gave an acetyl content of 4.61% and a biological activity of 188 units per mgm. It decreased rapidly to 138 units per mgm. in four weeks' time. The sample showing an acetyl content of 4.44% also showed a more intense biological activity when first tested.

Hurd, Cantor, and Roe (3) found that traces of sulphuric acid acted as a catalyst for the acetylation of simple sugars by this method. However, we found that the presence of sulphuric acid may cause inactivation of the heparin. At pH 3.0, 10% of the biological activity was lost; at pH 1.3, a compound was obtained having 4.06% acetyl but only 4% of the biological activity. The sulphuric acid was therefore omitted in the preparation.

Properties of the Acetyl Derivative of Heparin

The compound was stored for a month *in vacuo* over calcium chloride without change in acetyl or biological activity. The effect of temperature on neutral solutions of the compound is shown in Table I. Heating a neutral solution at 70° C. for 30 min. caused no loss in potency of either heparin or the acetyl compound. However, the acetyl compound lost more than half its acetyl by this treatment. Autoclaving for one hour at 15 lb. pressure caused no decrease in anticoagulant potency of heparin itself. There was a slight decrease in the value for the acetyl heparin, and a marked loss in the acetyl content. The effect of pH on the biological activity of heparin is

TABLE I

EFFECT OF TEMPERATURE ON NEUTRAL SOLUTION OF HEPARIN AND ACETYL HEPARIN

Substance	Treatment	Biological potency/mgm.	Acetyl, %
Heparin	—	124	0.57
Acetyl heparin	—	131	4.02
Heparin, 3 mgm./ml.	70° C. for one-half hour	130	—
Acetyl heparin, 3 mgm./ml.	70° C. for one-half hour	122	1.58
Heparin, 4 mgm./ml.	Autoclave for one hour[1]	134	—
Acetyl heparin, 4 mgm./ml.	Autoclave for one hour[1]	109	1.31

[1] *15 lb./sq. in.*

shown in Table II. Samples (30 mgm.) of heparin and of acetyl heparin were placed in 25 ml. flasks, 10 ml. of water acidified with hydrochloric acid was added to each; and the flasks placed in a water-bath at 50° C. for two hours. The contents of the flasks were then taken to dryness over calcium chloride *in vacuo* and assayed. Both heparin and acetyl heparin rapidly lose their biological activity in acid solution. As apparent, the acetyl compound is the less stable below pH 2.0.

TABLE II

EFFECT OF pH ON THE BIOLOGICAL ACTIVITY OF HEPARIN AND ON ITS ACETYL DERIVATIVE

pH	Biological activity in units/mgm.	
	Heparin, 3 mgm./ml.	Acetyl derivative of heparin, 3 mgm./ml.
1.04	18.7	3.7
1.39	36.9	5.3
2.01	67.2	69.5
3.04	84.4	109.4
3.99	107.2	117.7

Note.—Temperature, 50° C. Time, two hours.

Miss A. G. Macdonald kindly tested a sample of acetyl heparin for its effect on the clotting time of two dogs when injected intravenously as described by Jaques and Macdonald (6). No difference in response was obtained for the acetyl heparin as compared with the original heparin.

Investigations have not been made of the site of attachment of the substituted acetyl. The instability of the linkage makes it doubtful that the acetyl is joined to nitrogen as in glucosamine. Further, it is evident from the results of Charles and Scott, and of Wolfrom, Weisblat, Karabinos, McNeely, and McLean, that in heparin the amino group of glucosamine is substituted, although the substitution does not form as strong a bond as that of acetyl in glucosamine. Formation of acid anhydrides with the neutral sodium salt of heparin appears unlikely. This leaves only the hydroxyl groups of the sugars for substitution. When all the sulphuric acid residues and oxygen bridges in the four-hexose unit are allowed for, five to seven hydroxyl groups remain (10). It is presumed that substitution occurs at these carbons. It would be of interest to study this point in more detail. Whether heparin as it occurs naturally is acetylated, is not known. Certainly, in view of the lability of the acetyl group, it would be lost during the usual procedures of isolating heparin from tissue.

Acknowledgment

We wish to take this opportunity to express our appreciation of the interest and support of Prof. C. H. Best.

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COMPOUND FORMATION IN THE SYSTEM UROTROPINE - ACETIC ACID

I. THE PHASE DIAGRAM[1]

By K. K. Carroll[2] and R. H. Wright[3]

Abstract

The freezing point diagram has been plotted for mixtures of acetic acid and urotropine containing 0 to 42% urotropine. Formation of a solid compound melting at 24.8° C., and having the approximate composition $(C_6H_{12}N_4)_3 \cdot (C_2H_4O_2)_{13}$ is indicated. Repeated purification of the materials failed to shift the curve maximum to the expected ratio of 1 mole of urotropine to 4 moles of acetic acid.

Materials and Experimental Procedure

The urotropine was a commercial preparation supplied by Dr. C. A. Winkler of McGill University. It was twice crystallized from 95% ethanol and dried in a desiccator over concentrated sulphuric acid.

C.p. glacial acetic acid was distilled from potassium dichromate, and the distillate fractionally frozen until the residue froze at or above 16.5° C.

In the determination of the cooling curves, the solutions of urotropine in acetic acid were placed in a double-walled Pyrex tube fitted with a thermometer and ring-shaped glass stirrer. The approximate freezing point was first determined, then the cooling bath was adjusted to 4° to 5° C. lower for the actual measurement of the cooling curve. The freezing point diagram was constructed from the observed breaks and arrests in the cooling curves.

Results and Discussion

A summary of the results is given in Table I, and the freezing point diagram is shown in Fig. 1.

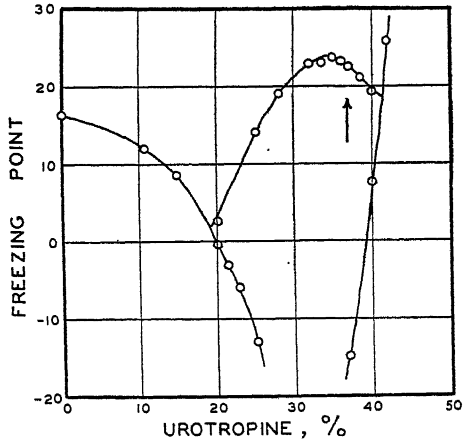

Fig. 1. *Freezing point diagram.*

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[2] *Present address: Department of Endocrinology, McGill University.*

[3] *Present address: Head, Division of Chemistry, British Columbia Research Council.*

The diagram shows the formation of a solid compound with a congruent melting point. Its composition, as indicated by the maximum in the curve, is approximately $(C_6H_{12}N_4)_3 \cdot (C_2H_4O_2)_{13}$. The maximum is fairly sharp; this indicates that there is some association in the liquid state as well.

TABLE I

Urotropine, %	Freezing point, ° C.	Solid phase
0	16.5	Acetic acid
10.7	12.0	" "
14.8	8.5	" "
—	2.4	Eutectic
20.0	−0.4	Acetic acid
20.0	2.6	Compound
21.4	−3.0	Acetic acid
22.8	−6.0	" "
25.0	−13.0	" "
25.0	14.2	Compound
28.0	19.2	"
32.0	23.0	"
33.5	23.1	"
35.0	23.8	"
36.0	23.3	"
36.85	22.8	• "
36.85	−15.0	Urotropine
38.5	21.2	Compound
40.0	19.4	"
40.0	7.7	Urotropine
—	18.9	Eutectic
42.0	26.0	Urotropine
• (The following measurements were made with anhydrous calcium sulphate added.)		
35.0	24.1	Compound
36.0	23.5	"
36.85	23.2	"
(The following measurements were made with acetic acid, m.p. 14.7° C. containing 0.9% added water.)		
32.0	20.0	Compound
33.5	20.5	"
35.0	20.3	"
36.0	20.1	"

The system shows a marked tendency to supercool and the compound does not crystallize unless the solution is seeded. No solid separated from a 32.5% mixture after two hours at −17° C. A solid did separate, however, when such a mixture was left in the cooling bath overnight. Because of this supercooling, it was possible to follow the freezing point diagram below the eutectic points.

The solid separating from solutions high in urotropine appeared to be urotropine rather than another acetate. It separated more readily when the solution was seeded with urotropine, and the crystals when filtered and dried with filter paper decomposed from 210° to 260° C. in a melting point tube. More than 42% urotropine could not be dissolved in acetic acid, and heating to higher temperatures caused decomposition.

The presence of four nitrogen atoms in urotropine makes the formation of a tetra-acetate seem logical, and the maximum in the curve is near the required composition. At the same time, it does not coincide exactly with the required composition: the arrow in Fig. 1 shows the composition corresponding to urotropine tetra-acetate. This anomaly was investigated in some detail.

Thus, as a further purification, the acetic acid was frozen out repeatedly until it melted at 16.7° C.; further fractional freezing did not raise the melting point. A solution made from this acid and containing 36.85% urotropine had a freezing point of 23.0° C., which was lower than that of a 35.0% solution made with acetic acid of melting point 16.5° C.

Again, the purified urotropine was analysed for formaldehyde and ammonia by the method of Carmack (1). Found: formaldehyde, 127.6%; ammonia, 48.59%. Calc.: formaldehyde, 128.5%; ammonia, 48.60%.

This agreement is reasonably good and indicates that there is no significant amount of impurity in the urotropine. Also, when the urotropine was further purified by sublimation *in vacuo* at 160° to 180° C., the freezing points of solutions containing 35.0 and 36.85% urotropine respectively were unchanged. The same results were obtained when the urotropine was purified by crystallization from absolute methanol. It seems unlikely from these results that the discrepancy was caused by impurity in the urotropine.

The effect of water as a third component was shown by a series of solutions containing 0.9% added water. This displaced the curve downward about 3°C. and flattened it somewhat, and the peak was shifted to approximately 33.5% urotropine. Thus it was thought that an absolutely anhydrous medium might show a maximum at 36.85% urotropine. Anhydrous calcium sulphate was added to a normal series of solutions in an effort to remove traces of water without interfering with the freezing points. In such a series, the freezing points were all slightly higher than they were before, but there was no perceptible shift in the peak towards 36.85% urotropine.

In a further attempt to show the composition of the compound, crude urotropine was dissolved in reagent acetic acid (1 mole in 4) to give about 400 gm. of solution. This was seeded with the compound and allowed to freeze slowly so that large crystals formed. The mixture was kept in a stoppered separatory funnel and the unfrozen liquid drained off. The crystals were then melted and allowed to freeze again slowly and the residual liquid again removed. This process was repeated 10 times. The final crystals melted at 24.8° C. They were analysed for formaldehyde and ammonia contents and the results expressed as the percentage of urotropine. Found: formaldehyde, 33.83%; ammonia, 34.52%.

It was further found that the presence of urotropine does not interfere in the titration of acetic acid with sodium hydroxide using phenolphthalein. Titration of a sample of the above crystals melting at 24.8° C. gave 65.52% acetic acid corresponding to 34.48% urotropine. This is in good agreement with the formaldehyde and ammonia analyses.

In all the experiments, higher melting points were obtained with solutions containing 34 to 35% urotropine rather than those containing 36.85%, which corresponds to the more plausible tetra-acetate formula. An impurity would be expected to lower the whole curve and could also displace the maximum. However, no direct evidence for such an impurity was obtained and its presence remains purely hypothetical.

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COMPOUND FORMATION IN THE SYSTEM UROTROPINE - ACETIC ACID

II. RAMAN SPECTRUM MEASUREMENTS[1]

By K. K. Carroll[2] and R. H. Wright[3]

Abstract

The Raman spectrum of a solution of urotropine in acetic acid (1 mole in 4) has been measured. The results are interpreted as indicating partial combination of the two in the liquid state. The presence of ammonium nitrate in amounts up to 1% caused no observable change in the Raman spectrum. Increasing the temperature of the solution containing ammonium nitrate to 50° to 60° C. resulted only in a uniform darkening of the lines.

It has previously been shown (1) that urotropine and acetic acid form a solid compound melting at 24.8° C. The present work was designed to reveal the existence of combination in the liquid state. Information was also desired on the effect of small amounts of ammonium nitrate.

Materials, Apparatus, and Experimental Procedure

The materials were purified as in the previous work (1).

A Bausch and Lomb constant deviation glass spectrograph (*f* 17.2) was used in photographing the Raman spectra.

The source was a coiled mercury discharge lamp (30 coils) which surrounded a Raman tube consisting of two concentric glass tubes, the outer one serving as a jacket for holding filters.

The 4358 mercury line was used as the exciting radiation. Two filters were used for isolating this line. The 4046 mercury line was absorbed by filling the outer jacket of the Raman tube with a 25% solution of nitrobenzene in ethanol (2 mm. layer). The 4916 mercury line and the continuous background between it and 4358 were reduced by a gelatin filter stained with crystal violet. This was prepared by dipping the Raman tube in a 12% solution of gelatin at 50° to 60° C., allowing it to dry, and then dipping it in a 0.6% solution of crystal violet in water, and again allowing it to dry.

The exposures were of 90 hr. duration. The mercury lamp generated enough heat to maintain the Raman tube at 50° to 60° C. unless it was kept at room temperature by means of an electric fan. (This was done except where otherwise stated.)

The comparison spectrum consisted of the superimposed lines of mercury, helium, and argon discharge tubes.

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[1] *Manuscript received November 6, 1946.*

Contribution from the Department of Chemistry, University of New Brunswick, Fredericton, N.B. This work was carried out with the assistance of a grant from the National Research Council.

[2] *Present address: Department of Endocrinology, McGill University.*

[3] *Present address: Head, Division of Chemistry, British Columbia Research Council.*

The frequency separation of the Raman lines was measured by a projection apparatus as suggested by Hibben (2). The apparatus was calibrated by measuring the linear separation of the lines in the comparison spectrum and plotting against the known separation in wave numbers. The wave number separation of the Raman lines was read directly from this graph after the linear separation had been measured. The relative intensities of the lines were judged visually on a 0 to 10 scale.

All photographs were taken on Eastman spectrographic plates (Type 103-F). Development was for five minutes at 20° C. using Eastman formula D-19 developer, and the plates were fixed for 15 min. with Eastman F-5 acid-hardening, fixing solution.

Results and Discussion

The Raman spectra of acetic acid and of urotropine, both crystalline and in aqueous solution, have been measured by a number of investigators (3). The spectrum of acetic acid was repeated to give an estimate of the light-gathering power of the spectrograph and to check the method of calibration. With the apparatus available, it was not possible to observe the Raman spectrum of the urotropine – acetic acid compound in the solid state.

A solution of urotropine in acetic acid (mole ratio 1:4) was photographed with and without the addition of 0.32% of ammonium nitrate. No difference was observed in the two spectra. By raising the temperature to 50° to 60° C., 1.08% of ammonium nitrate could be kept in solution, but again no difference was observed apart from a general darkening of the lines.

The photographs of the Raman spectra of acetic acid and of the urotropine – acetic acid solution are reproduced in Fig. 1. The Raman shifts and relative intensities of the lines are given in Table I. Fig. 2 gives a graphical comparison of these results with those of other workers.

TABLE I

EXPERIMENTAL RESULTS

The numbers give the separations of the Raman lines from the exciting line, expressed in wave numbers. The figures in parentheses indicate the relative intensities. *b* = broad; *sb* = medium broad; *d* = diffuse.

Acetic acid: 450 (½); 624 (2); 899 (5); 1354 (½*b*); 1436 (2*b*); 1670 (2*b*); 2945 (10); 2986 (½); 3028 (½).

Urotropine + acetic acid (1:4 moles): 457 (2); 507 (1); 616 (½); 703 (0?); 792 (3*b*); 891 (4*sb*); 941 (0); 1025 (1); 1071 (0?); 1356 (4); 1451 (4*b*); 1721 (1*d*); 2940 (10*b*); 3003 (6*b*).

PLATE I

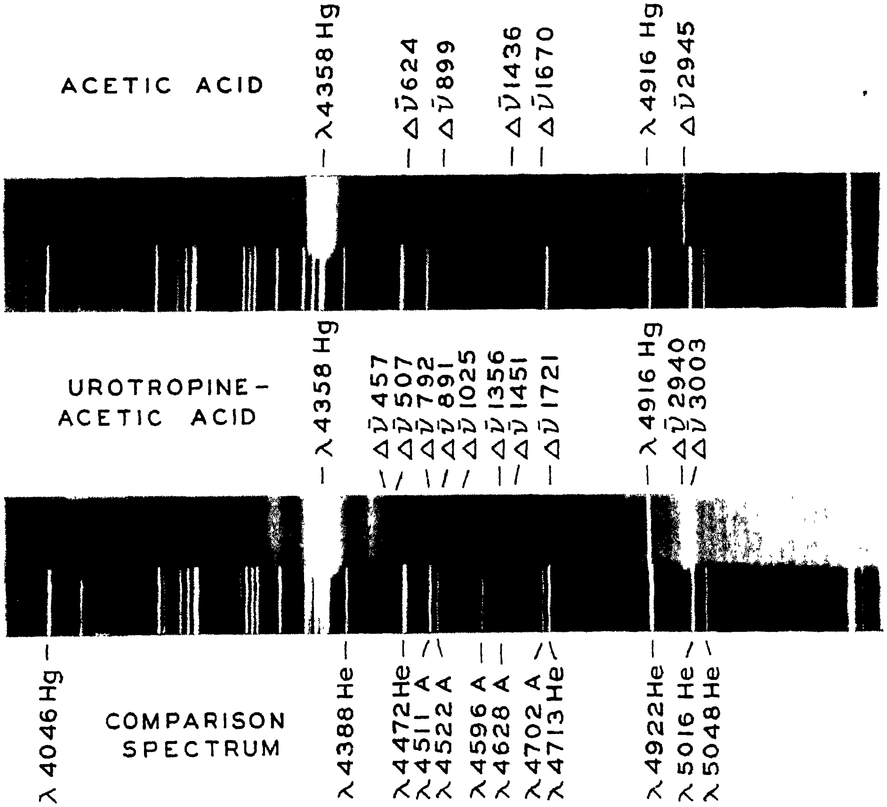
ACETIC ACID
λ 4358 Hg
Δν̄ 624
Δν̄ 899
Δν̄ 1436
Δν̄ 1670
λ 4916 Hg
Δν̄ 2945
UROTROPINE-ACETIC ACID
λ 4358 Hg
Δν̄ 457
Δν̄ 507
Δν̄ 792
Δν̄ 891
Δν̄ 1025
Δν̄ 1356
Δν̄ 1451
Δν̄ 1721
λ 4916 Hg
Δν̄ 2940
Δν̄ 3003
COMPARISON SPECTRUM
λ 4046 Hg
λ 4388 He
λ 4472 He
λ 4511 A
λ 4522 A
λ 4596 A
λ 4628 A
λ 4702 A
λ 4713 He
λ 4922 He
λ 5016 He
λ 5048 He

FIG. 1

The results show that nearly all the lines obtained in the urotropine – acetic acid solution correspond with lines of either acetic acid or urotropine. There are two notable exceptions.

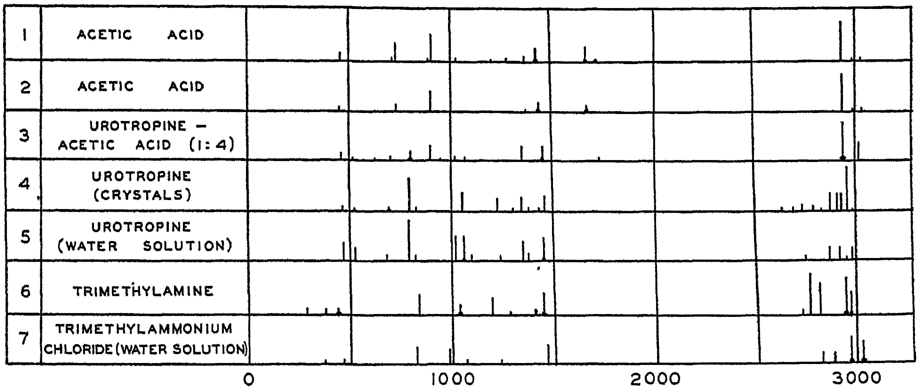

FIG. 2. *The values in 2 and 3 are from the present work. The remainder are taken from Kohlrausch (3).*

The line $\Delta\bar{\nu}$ 1666-1670 of acetic acid is not present in the solution but is replaced by a fainter and more diffuse line at $\Delta\bar{\nu}$ 1721. A similar change has been observed when acetic acid is diluted with a number of solvents (2). The line at $\Delta\bar{\nu}$ 1666 is generally ascribed to the $-C=O$ group in the dimeric molecules of acetic acid, and the $\Delta\bar{\nu}$ 1700 line to the monomeric form (2). The presence of either of these lines is evidence that the liquid contains some free acetic acid. In acetates, such as sodium and ammonium acetate, these frequencies disappear and a strong line is found in the vicinity of $\Delta\bar{\nu}$ 1400 (3). Urotropine itself has several strong lines in the vicinity of $\Delta\bar{\nu}$ 1400, so that it was not possible to detect this line in the present case.

The second important change in the spectrum is the disappearance of several urotropine lines near $\Delta\bar{\nu}$ 2900 and the appearance of a single heavy and rather broad line at $\Delta\bar{\nu}$ 3003. This line may be due to an N-H vibration in a urotropine acetate. Lines due to N-H vibrations usually occur in the range $\Delta\bar{\nu}$ 3200-3400, but smaller separations are usual in ammonium and substituted ammonium salts (3). For example, dimethyl- and trimethylamine hydrochlorides give lines at $\Delta\bar{\nu}$ 3040 and the propylammonium ion gives a line at $\Delta\bar{\nu}$ 2980. The Raman spectra of trimethylamine and trimethylamine hydrochloride are given for comparison in Fig. 2. Urotropine hydrochloride has been studied in the crystal form by Krishnamurti (4), who gives the values 444 (1), 713 (3), and 856 (1) with no long frequencies. It is possible that lines of large frequency separation were present but were not observed.

Several other changes are observable in the new spectrum, such as the disappearance of a urotropine line at $\Delta\bar{\nu}$ 1234, but since such lines have not been associated with any particular vibration in the molecule, it is difficult to interpret these changes.

In general, the results support the conclusion that urotropine combines with acetic acid in the liquid state as well as in the solid state.

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QUANTITATIVE ESTIMATION AS ACETIC ACID OF ACETYL, ETHYLIDENE, ETHOXY, AND α-HYDROXYETHYL GROUPS[1]

By R. U. Lemieux[2] and C. B. Purves[3]

Abstract

Kuhn and L'Orsa's method for estimating terminal methyl and similar groups was based on the recovery of the acetic acid formed when such units were oxidized with hot concentrated chromic acid solution. The method has now been reduced to the semimicro scale and refined to the point where good analyses for acetyl, ethylidene, ethoxy, and α-hydroxyethyl groups in a variety of substances are obtained. Acetylated triphenylmethyl cellulose ethers, which do not seem amenable to customary acetyl analyses, give good results by the present procedure.

Introduction

During an extension of published work on the acetylation of cellulose trityl (triphenylmethyl) ether (5, 11, 12), standard methods of acetyl analysis proved to yield low results. Those tried were the sodium methylate saponification – *p*-toluenesulphonic acid – methanol distillation method of Cramer, Gardner, and Purves (1), the modification of the Ost distillation technique by Genung and Mallatt (2), and saponification in a homogeneous medium as described by Malm, Genung, Williams, and Pile (9). Although all three methods gave concordant and correct results in the absence of the trityl ether unit, in its presence each, although often fairly reproducible in duplicate estimations, was low by a variable amount. Attempts made on samples containing added triphenylmethyl carbinol to determine the cause of these aberrations led to no definite conclusion. In these circumstances attention was given to the oxidations of organic substances by Kuhn and L'Orsa (7), who employed a hot concentrated aqueous solution of chromium trioxide. These authors found that in many cases a steam distillation of the oxidizing mixture recovered acetyl, ethoxy, and terminal methyl groups as acetic acid, the yield of acetic acid often being more than 85% of theory. Their results were confirmed, for terminal methyl groups in the lignin series, by MacGregor, Evans, and Hibbert (8). The present article describes a semimicro adaptation of the estimation, which gave practically quantitative results. Although in blank runs the acidity of the distillate varied from 0.5 to 1.3 ml. of 0.02 *N* alkali with slight variations in operating conditions, for a given apparatus and given reagents this blank was in a fixed ratio to the oxidizing equivalent of the distillate in terms of 0.02 *N* sodium thiosulphate solution. Ratios of 1.33 to 1, and 0.91 to 1, for example, were observed with two sets of equipment used at different times. This blank acidity was presumably caused by

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[1] *Manuscript received December 7, 1946.*

Contribution from the Division of Industrial and Cellulose Chemistry, McGill University, Montreal, Que. From a thesis presented to the Faculty of Graduate Studies and Research by R. U. Lemieux in September 1946 in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] *Holder of Studentships under the National Research Council of Canada, 1944-45, 1945-46. Present address: Department of Chemistry, University of Saskatchewan, Saskatoon, Sask.*

[3] *E. B. Eddy Professor of Industrial and Cellulose Chemistry, McGill University.*

volatile impurities in the reagents and by the entrapment of traces of chromic acid in the distillate. Knowledge of the factor relating number of cubic centimetres of alkali to number of cubic centimetres of thiosulphate in the blanks made it possible to dispense with separate blank determinations in routine estimations with the same equipment and reagents.

Description of the Method

Reagents

1. Aqueous 30% chromium trioxide,
2. Carbon dioxide-free 0.020 *N* sodium hydroxide,
3. Standard 0.020 *N* sodium thiosulphate,
4. Iodate-free potassium iodide,
5. Aqueous 10% sulphuric acid,
6. Sodium bicarbonate,
7. Indicator solutions: phenolphthalein, 1% amylose.

Procedure

A 15 to 50 mgm. sample (depending on the amount of acetic acid produced) was weighed into a 100 ml. round-bottomed flask equipped with a ground glass joint (Fig. 1). The sample was covered with 10 ml. of the 30% chromic

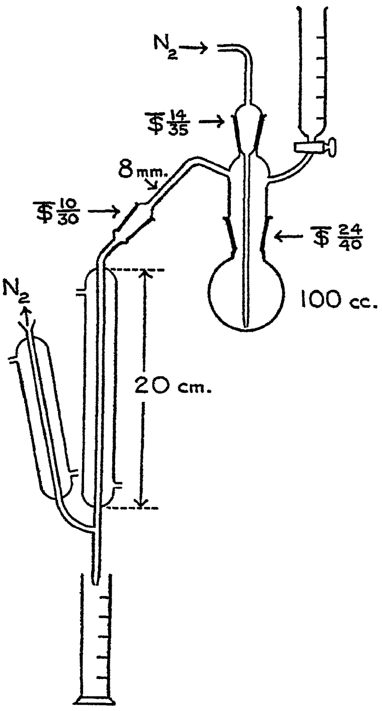


Fig. 1.

acid solution, the flask was two-thirds immersed in an oil-bath, the apparatus (Fig. 1) was assembled, and nitrogen gas was passed through it at a rate of one to two bubbles per second. The temperature of the bath was then raised to 155° C. within one-half hour by means of a hot-plate and was maintained at this figure until the end of the determination. Too rapid an initial rise in temperature resulted in high blanks. Distillation began at 135° to 140° C. and, as successive 5 ml. volumes of distillate collected in the 50 ml. graduate, 5 ml. volumes of distilled water were added to the still from the 50 ml. graduated dropping funnel. This procedure was continued until 50 ml. of water had been added and 55 ml. of a very faintly yellow distillate had been collected. The condenser was then detached from the still-head and both arms of the former were washed with distilled water, the washings being collected in a 250 ml. Erlenmeyer flask. The contents of the graduate was then quantitatively transferred to the same flask and the combined solution was titrated with standard carbon dioxide-free 0.020 *N* sodium hydroxide solution until the end-point just began to fade (phenolphthalein indicator). The liquor was then brought to a boil to remove carbon dioxide, cooled to room temperature under the cold water tap, and the titration continued until the pink coloration remained stable for 10 sec. Note was taken of the volume, x, of standard alkali used. Approximately 0.5 gm. of sodium bicarbonate was then added, followed by 10 ml. of 10% sulphuric acid, and, after carbon dioxide evolution had ceased, by 1 gm. of potassium iodide. The flask was stoppered, shaken, and kept in the dark for five minutes, after which time the liberated iodine was titrated with 0.020 *N* sodium thiosulphate. This titration, y cc., when multiplied by the empirical factor K appropriate to the particular apparatus and reagents in use, gave the acid equivalent *not* caused by acetic acid. The acetic acid equivalent was therefore $(x - Ky)$ cc. of 0.02 *N* alkali.

Two and one-half hours was required for the estimation.

Table I shows that the oxidation quantitatively recovered the terminal methyl groups in the first two compounds as acetic acid and is therefore valid for primary desoxy groups in carbohydrates. Since the chromic acid oxidation does not demand the presence of an unsubstituted 1,2-glycol unit adjacent to the methyl group, it is certainly more widely applicable than the periodate-oxidation technique developed by Nicolet and Shinn (10), and is probably just as convenient. Determinations of the ethylidene group in a sample of monoethylidene methyl-α-glucopyranoside prepared by Hill and Hibbert (6), and of the ethoxy groups in a technical ethylcellulose, were also successful. The method should find application for group analyses in ethylidene derivatives of polyhydroxy substances and for the estimation of ethoxy in presence of methoxy groups. Analyses for acetyl content in the absence of trityl units agreed well both with theory and with the results of other standard methods. The present procedure also gave a satisfactory result with 6-trityl methyl-α-glucopyranoside triacetate.

TABLE I

ACETYL AND TERMINAL METHYL GROUP ESTIMATIONS

Compound	Sample, mgm.	Correction blank, *Ky* ml.[1]	'Total acetyl'	
			% Calc.	% Found
Rhamnose hydrate	37.5	0.45	23.6	23.2
Isorhamnose tetraacetate	19.9	0.80	64.8	64.5
Monoethylidene methyl-α-glucoside	52.4	0.36	19.6	19.5
Ethylcellulose[2]	50.4	0.48	26.4	26.3
Glucose pentaacetate	24.8	0.80	55.0	55.0
Methyl-α-glucoside tetraacetate	21.3	0.77	47.5	47.5
Cellulose acetate[3]	29.1	0.60	38.6	38.8
6-Trityl methyl-α-glucoside triacetate[4]	49.3	0.82	23.0	23.6
	54.1	0.55	23.0	23.4
Trityl cellulose acetate[5]	70.3	1.33	17.4[5]	17.5
	55.4	0.81	—	17.2

[1] *Ml. of 0.02 N caustic soda.*

[2] *Presented by the Hercules Powder Co. Sample X 2167-12; of 27.6% ethoxy content by standard alkoxyl estimation.*

[3] *Presented by the Eastman Kodak Co. An acetone soluble grade with 38.6% acetyl.*

[4] *Old sample of Gladding and Purves (3). M.p. 145° to 147° C. (uncorr.) instead of m.p. 142° to 145° C. (corr.).*

[5] *See Table II.*

TABLE II

ACETYL CONTENT OF TRITYL CELLULOSE ACETATES

Trityl cellulose	Acetylated products[1]				Other acetyl analyses
	% Trityl[2]	% Acetyl	Moles trityl[3]	Moles acetyl[3]	
I	50.5	15.3	0.98	1.67	10.7[4]
XI	51.7	13.9	0.99	1.49	9.3, 12.2[5]
XI	51.7	14.5	1.00	1.55	—
XI	49.5	18.0	0.99	2.01	—
XI	50.2	17.4[8]	1.02	1.98	14.0, 14.6[6]
—[7]	52.3	13.8	1.01	1.51	9.6, 9.2[4]

[1] *With acetic anhydride, or acetyl chloride, in pyridine for various times at various temperatures.*

[2] *Analyzed by Hearon, Hiatt, and Fordyce method (4).*

[3] *For calculation see text.*

[4] *Cramer, Gardner, and Purves method (1).*

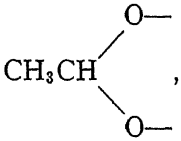
[5] *Method of Malm, Genung, Williams, and Pile (9).*

[6] *Genung and Mallatt method (2).*

[7] *Prepared by Dr. V. R. Grassie.*

[8] *See Table I.*

Table II summarizes the analyses of a series of acetates derived from three different preparations of cellulose monotrityl ether. The molar substitutions per glucose unit of trityl and acetyl were readily calculated from the percentage figures by means of a simultaneous equation. Since acetylation for various times in pyridine solution was not likely to affect the trityl unit, the fact that the trityl substitution remained close to the correct value of unity while the acetyl content varied is good evidence that the analyses for acetyl, as well as for trityl, are reliable. Other analyses for acetyl, shown to the right of the table, were low.

Consideration of the above results, together with those of the previous investigators (7, 8) shows that the chromic acid oxidation method must be restricted to terminal methyl groups that oxidize quantitatively to acetic acid. This condition is satisfied when the carbon atom adjacent to the methyl group is directly linked to at least one oxygen atom, as in $CH_3CH_2—O—$,  $CH_3CH\left\langle\begin{matrix}O—\\O—\end{matrix}\right.$, $CH_3CHOH—$, or $CH_3COO—$. The method fails with compounds such as toluene, cellulose propionates and butyrates, in which the adjacent carbon atom is not substituted by oxygen, because the production of acetic acid from the terminal methyl group is not quantitative. Such compounds constitute interfering substances. Interference was also caused by the allyl ether group, $CH_2=CH—CH_2—O—$, which was found by Dr. L. A. Cox to yield a small amount of volatile acid in the chromic acid oxidation.

Acknowledgment

This research was partly financed by grants from the National Research Council of Canada. One of us (R. U. L.) takes this opportunity of thanking the same organization for two studentships and for sundry maintenance grants awarded to him.

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PRODUCTION AND PROPERTIES OF 2,3-BUTANEDIOL

XXIV. THE CYCLIC SULPHITES OF *meso-* AND *levo*-2,3-BUTANEDIOL[1]

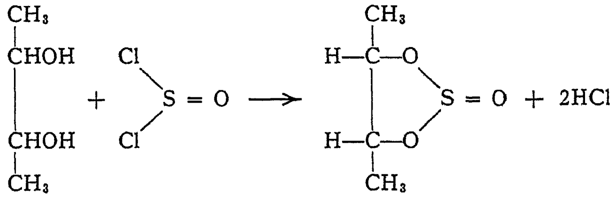
BY FLORENCE M. ROBERTSON[2] AND A. C. NEISH[2]

Abstract

levo-2,3-Butanediol reacts spontaneously with thionyl chloride to give good yields of its cyclic sulphite (b.p. 177° to 178° C.). This ester is optically active ($[\alpha]_D^{25} = 19.9°$) and can be hydrolyzed by dilute hydrochloric acid to pure *levo*-2,3-butanediol and sulphurous acid. The cyclic sulphite of *meso*-2,3-butanediol (b.p. 188° to 189° C.) was also prepared.

Introduction

Thionyl chloride is frequently used for the replacement of a hydroxyl group by a chlorine atom (2, p. 84). In this laboratory it was used in an attempt to replace the hydroxyl groups of *levo*-2,3-butanediol, to form the chlorohydrin. Instead of the expected reaction, however, it was found that the cyclic sulphite of *levo*-2,3-butanediol formed as follows:



The ester thus obtained was optically active; on acid hydrolysis pure *levo*-2,3-butanediol was recovered, showing complete retention of configuration. *meso*-2,3-Butanediol also reacted with thionyl chloride to give an isomeric sulphite. The properties of these compounds are given in Table I. They are colourless liquids, immiscible with water, but easily hydrolyzed by acids and alkalis. The specific rotation of the *levo*-isomer is extremely sensitive to temperature changes, varying from +19.80° at 24.5° C. to +21.31° at 32° C. Because these compounds have a greater difference between their boiling points (11° C.) than any other known derivatives of the 2,3-butanediols, they might prove useful in the separation of *dextro-* or *levo*-2,3-butanediol from the *meso*-isomer.

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[2] *Biochemist, Industrial Utilization Investigations.*

A compound analogous to these was prepared by Schiller (9) from diethyl tartrate and thionyl chloride, and other workers have reported compounds of the type $(RO)_2SO$ as reaction products of thionyl chloride with alcohols (3, 5, 8). Recently Kolfenbach *et al.* (4) have prepared a cyclic carbonate of 2,3-butanediol by reaction with phosgene. It is possible that this reaction is general when 2,3-butanediol is treated with acid chlorides.

TABLE I

PHYSICAL PROPERTIES OF THE CYCLIC SULPHITES OF 2,3-BUTANEDIOL

——	Sulphite of *levo*-2,3-butanediol	Sulphite of *meso*-2,3-butanediol
Boiling point, ° C.	177–178	188–189
Density, d_4^{25}	1.192	1.211
Refractive index, 25° C.	1.4296	1.4368
Specific rotation, $[\alpha]_D^{25}$	+ 19.92°	—

Experimental

Materials and Methods

levo-2,3-Butanediol, containing about 3% water, was obtained from the pilot plant fermentation of wheat by *Aerobacillus polymyxa* (6). The *meso*-isomer was prepared by the fractional distillation through a Stedman column of crude *meso-dextro* glycol obtained in the pilot plant from the fermentation of molasses by *Aerobacter aerogenes* (1). The purified material had an optical rotation of +0.20°. Eastman's practical grade thionyl chloride was used.

Carbon and hydrogen values were obtained from combustion of the compounds by Liebig's method, lead chromate and silver ribbon being added to the packing to remove sulphur.

To determine the sulphur, 200-mgm. samples of the compounds were refluxed with 15 ml. of 5 *M* nitric acid for half an hour; the sulphate thus formed was precipitated as barium sulphate and weighed according to the usual procedure. The ease with which the sulphur was oxidized was strong evidence for the proposed cyclic sulphite structure; few organic compounds yield their sulphur under such mild conditions.

The compounds decomposed slowly on standing and in every case the analyses were performed on freshly distilled material.

Cyclic Sulphite of meso-2,3-Butanediol

Thionyl chloride, 160 ml. (2.2 moles) was added dropwise to 180 ml. of *meso*-2,3-butanediol (2 moles) in a 1-litre, three-necked flask equipped with a dropping funnel, glycerol-sealed stirrer, and reflux condenser. The reaction mixture slowly turned dark brown. Although at first heat was evolved, later the reaction mixture spontaneously became cool, and after all the thionyl chloride had been added, the temperature had dropped to −1° C.* Stirring was continued and the flask was gradually heated to drive off as much hydrogen chloride gas as possible. The reaction mixture was distilled through a column of glass helices. A small amount of yellow material distilled over at a low temperature. The yield of the sulphite (collected from 182° to 189° C.) was about 212 gm. (78% yield). Calc.: C, 35.30; H, 5.88; S. 23.53%. Found: C, 35.44, 35.49; H, 6.03, 6.04; S, 23.70, 23.56%.

Cyclic Sulphite of levo-2,3-Butanediol

The *levo*-compound was prepared in the same way as the *meso*-compound. The yield of product collected from 170° to 178° C. was 190 gm. (70% yield). Calc.: C, 35.30; H, 5.88; S, 23.53%. Found: C, 35.23, 35.25; H, 5.80, 5.91; S, 23.44, 23.26%.

Hydrolysis of levo-2,3-Butanediol Cyclic Sulphite

Sixty-eight grams (0.5 moles) of the sulphite was heated with an equal volume of 0.5 *N* hydrochloric acid in a 500-ml., three-necked flask equipped with a stirrer, a reflux condenser, and a capillary. A stream of air was passed through the reaction mixture to carry off the liberated sulphur dioxide. After about four hours, when only a slight milkiness remained, the reaction mixture was neutralized to the phenolphthalein end point with 5 *N* sodium hydroxide solution, cooled, and filtered to remove sodium chloride crystals. The filtrate was extracted with ether in a continuous extractor for about 40 hr. Fractional distillation of the ether extract yielded 42.7 gm. of *levo*-2,3-butanediol. When allowance was made for the fact that only 97% of the diol was extracted in the apparatus used, the yield was 98%. The high optical rotation showed that the diol was the *levo*-isomer. The fraction from 176.5° to 177.0° C. had a rotation of −12.62°, and a later fraction boiling at 177.0° C., had a rotation of −13.03° (6). The 2,3-butanediol was identified by preparation of the di-(*p*-nitrobenzoate) which melted from 143.0° to 143.5° C. (corr.), as did the authentic derivative and a mixture of the two. No evidence of any other isomer was found by crystallization, and the optical rotation of a 4% solution of the derivative in dioxane indicated that it was 99 to 100% pure *levo*-derivative (7).

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* *The authors are unable to explain this unusual behavior. The reaction appears to proceed in two stages, the first exothermic, and the second, endothermic.*

THE OXIDATION OF METHANE AT HIGH PRESSURES

IV. EXPERIMENTS USING PURE METHANE AND COPPER, SILVER, ZINC, NICKEL, OR MONEL METAL AS CATALYSTS[1]

By E. H. Boomer[2] and S. N. Naldrett[3]

Abstract

Mixtures of methane and oxygen with some nitrogen were passed over catalysts of copper, silver, zinc, nickel, and Monel metal and the yields of methanol and other liquid products determined. The conditions of temperature, pressure, and rate of flow that were known to be best for a copper catalyst were used. Nickel and Monel metal appear to offer most promise. A massive form of catalyst appears to be better than a catalyst in the form of fine wire gauze for the maximum yield of liquid products.

Introduction

The present report is a continuation of a systematic investigation of the oxidation of methane at high pressures. Boomer and Thomas (3) passed mixtures of natural gas (substantially methane) and air in various proportions over catalysts and determined the effects of the variables: composition of the gas mixture, pressure, temperature, and space velocity. Similar investigations were carried out using mixtures of pure methane containing some nitrogen, and oxygen (4). Copper was the principal catalyst used but a few observations were made using catalysts of glass, nickel-chromium steel, or silver. They concluded that the action of the catalyst is twofold: (1) to provide a surface easily oxidized and reduced, and (2) to aid in the dissipation of the heat of the reaction. They believed gas phase reaction and lack of temperature control to be detrimental to the survival of useful liquid products.

In the investigation described in the present paper, the optimum conditions as found for a copper catalyst by Boomer and Thomas (3, 4) were adopted. Various metals have been used as catalysts in an attempt to find the best catalyst for the production and survival of methanol.

Experimental

The experimental methods were substantially the same as those described in previous reports; some modifications were introduced and are described in what follows.

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[2] *Late Professor of Chemistry, University of Alberta.*

[3] *Holder of University of Alberta Board of Governors Research Fellowship 1937-38. Present address: National Research Council, Ottawa.*

Materials

Natural gas from the Viking field near Edmonton was used. The composition of this gas, determined by ordinary combustion analysis, was approximately:

CH_4	90.8%
C_2H_6	3.5%
N_2	5.7%

Higher hydrocarbons such as propane were present in small amounts, and are included in the ethane figure. The gas had been artificially odorized with mercaptans and alkyl disulphides. The higher hydrocarbons and the sulphur compounds were pyrolyzed and the products of pyrolysis removed by a method that has been described (2). The composition of the gas produced was approximately 90% CH_4, 10% N_2; about 0.1 to 0.2% ethylene was still present. Analysis also indicated that the gas contained sulphur. The sulphur was apparently in an organic combination and was not absorbed in 40% potassium hydroxide solution, or by sodium hydroxide flakes, or by soda lime, or by triethanolamine. Ignition of the gas and absorption of the products of combustion in sodium carbonate solution as in a standard method of analysis (5) indicated a sulphur content of 0.3 to 0.5 grains per 100 cu. ft., which could not be reduced further by any amount of alkaline absorbents. Passing the gas through a condensing trap at about −100° C. reduced the sulphur content to an undetectable amount. However, for the large quantities of gas required for the preliminary survey of catalysts it was not practicable to make this purification. In any case, it would be valuable to find a catalyst that can resist poisoning by sulphur. Therefore, for the series of experiments reported here, it must be borne in mind that the catalysts are not operating at their optimum, and that further improvements can undoubtedly be made.

Oxygen as required was added to the gas from a commercial cylinder and the gas mixture was then compressed and pumped into the high pressure storage tanks.

Catalysts were used in three forms: as cylindrical pieces $\frac{1}{4}$ in. long cut from wire 0.08 in. diameter; as blocks about 3/16 in. square and 3/32 in. thick, and in the form of gauze. The reactor (the same one described in earlier investigations (3)) was tubular in shape, with a smaller tube, the thermocouple well, entering one end and projecting halfway into the reactor. Rings of gauze were punched out of a sheet to fit snugly into the reactor and pass over the thermocouple well. These rings were packed into the reactor up to the level of the end of the thermocouple well; the remainder of the reactor was packed with gauze disks. The gauze used was about 60 mesh, the diameter of the wire being 0.006 in.

The blocks and the gauze were originally copper. To obtain other surfaces, the copper blocks, or the disks and rings punched from copper gauze, were electroplated with the desired metal. In the form of blocks, copper and nickel surfaces were investigated; in the form of gauze, copper, silver, nickel, and zinc surfaces were examined. Monel metal was investigated as cylindrical pieces cut from wire.

In the cases of the surfaces obtained by electroplating copper gauze, plating did not occur at the points where the wires crossed, and copper was left exposed. The inside of the reactor also was copper-plated in all experiments but the total surface of copper was nevertheless slight in comparison with the surface of the metal being investigated.

Apparatus

The reaction system and its operation were the same as have already been described in detail (1, 3, 4) except in one regard—whereas in the investigation described in the earlier papers the methane and oxygen were stored separately under high pressure and mixed under high pressure as required in the course of an experiment, in the present investigation oxygen was added to the methane before compression. A single high pressure storage tank was used, and the pressure in the system was kept constant throughout an experiment by means of an automatic compression system as described earlier (4).

The catalyst was activated by alternate oxidation and reduction at the temperature at which the trial was to be made. Air was used to oxidize the catalyst; hydrogen and methanol vapor were used as a reducing agent.

The collection of samples and the methods of analysis were the same as those reported by Boomer and Broughton (1). As in the earlier investigations, the volume of in-gas was not measured directly, but was calculated from the measured amounts of off-gas and liquid products, using the element carbon as a reference. On the basis of a carbon balance, oxygen appeared to be lost, a phenomenon that has been observed in other investigations and has not yet been explained (4, 6).

Results and Discussion

A comparison of the effect of the block form of copper with the gauze form is presented in Table I. Experiments 1 to 5 with copper blocks were made under the same conditions as those for which Boomer and Thomas (4) obtained yields of about 60% methanol on the basis of percentage of carbon oxidized. The catalyst was reactivated after Experiment 2 in case the catalyst had become poisoned by oil contamination. The yield of methanol was increased somewhat as shown by Experiments 3 to 5 but was still below that obtained by Boomer and Thomas, probably owing to the sulphur content of the gas. Reactivation of the gauze catalyst after Experiment 7 also gave some improvement in yield of methanol. The yield appeared then to be steady in Experiments 8 to 10, but considerably below that obtained using copper blocks. This was not expected since a copper surface was known to be beneficial, and in these trials the area of copper surface had been greatly increased. However, the weight of copper used as catalyst in the form of gauze was only two-thirds the weight of the copper blocks. Hence, there was more free space in the reaction system when gauze was used, and, therefore, more opportunity for detrimental gas phase reactions. It is also probable

TABLE I

EXPERIMENTS COMPARING COPPER GAUZE AND COPPER BLOCKS

Experiment No.	1	2	3	4	5	6	7	8	9	10
Catalyst	Blocks	Blocks	Blocks	Blocks	Blocks	Gauze	Gauze	Gauze	Gauze	Gauze
Temperature, ° C.	450	450	450	450	450	450	450	450	450	450
Pressures, atm.	180	182	200	183	186	177	172	174	177	176
Off-gas flow, litres/min.	0.69	1.03	1.10	0.38	1.22	1.10	1.10	1.10	1.10	1.14
In-gas analysis:										
Olefins	0.45	0.45	0.45	0.45	0.40	0.22	0.22	0.11	0.11	0.17
O_2	5.5	5.6	5.8	5.8	5.7	6.3	6.0	6.0	6.1	5.7
CH_4	87.8	88.4	87.7	87.0	87.8	86.7	86.7	85.0	83.9	85.3
Off-gas analysis										
CO_2	1.25	1.20	1.30	1.55	1.30	1.72	1.84	1.60	1.50	1.50
Olefins	0.15	0.25	0.10	0.17	0.0	0.22	0.11	0.0	0.0	0.0
O_2	0.2	0.2	0.2	0.3	0.3	0.2	0.3	0.3	0.3	0.3
H_2	2.7	2.0	1.2	0.45	0.65	0.55	0.55	1.0	1.1	1.0
CO	1.5	1.5	0.65	0.2	0.4	0.90	0.45	0.7	0.7	0.6
C_2H_6	0.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CH_4	87.2	87.8	88.9	89.6	89.7	89.0	89.6	87.6	87.6	88.0
$\frac{\text{Volume in-gas}}{\text{Volume off-gas}}$	1.05	1.04	1.04	1.06	1.05	1.07	1.07	1.07	1.08	1.06
Condensate, gm./100 litres in-gas at N.T.P.										
Total	6.74	6.44	5.90	5.90	6.41	7.08	6.58	6.41	5.66	5.81
CH_3OH	1.80	1.90	1.85	1.74	1.84	1.02	1.02	1.33	1.32	1.15
CH_2O	0.033	0.022	0.025	0.042	0.035	0.086	0.086	0.048	0.048	0.049
HCOOH	0.044	0.032	0.028	0.024	0.031	0.022	0.026	0.033	0.031	0.034
H_2O	4.86	4.49	4.00	4.10	4.50	5.95	5.45	5.00	4.26	4.58
Alcohol in condensate, %	26.8	29.5	31.3	29.5	28.8	14.4	15.5	20.75	23.3	19.8
Total carbon oxidized, %	4.46	4.45	3.60	3.33	3.34	3.70	3.37	3.68	3.59	3.31
Yields, as % of total carbon burned to:										
CH_3OH	31.9	33.5	40.5	41.7	43.7	22.1	24.3	29.7	30.6	28.4
CH_2O	0.62	0.40	0.57	0.61	0.90	2.00	2.19	1.14	1.20	1.30
HCOOH	0.54	0.39	0.43	0.70	0.52	0.34	0.41	0.52	0.50	0.59
Total	33.06	34.29	41.50	43.01	45.12	24.44	26.90	31.36	32.30	30.29
Total inlet oxygen accounted for, %	106	99	83	87	91	100	100	96	81	93

that the surface temperature of the gauze was higher owing to the greater active area per unit mass of copper, and this decreased temperature control is probably responsible in part for the lower yields of methanol.

Table II gives the results of a series of experiments made to compare various metals as catalysts in the form of gauze. Experiments 11 to 13 using silver gauze gave less methanol than was obtained when copper gauze was used. Boomer and Broughton (1) and Boomer and Thomas (4) found silver to be

TABLE II

COMPARISON OF VARIOUS METALS IN THE FORM OF GAUZE

Experiment No.	11	12	13	14	15	16	17	18	19
Catalyst	Silver	Silver	Silver	Zinc	Zinc	Zinc	Nickel	Nickel	Nickel
Temperature, ° C.	450	450	450	450	450	450	450	450	450
Pressure, atm.	176	176	179	182	181	190	177	182	184
Off-gas flow, litres/min.	1.09	1.06	1.10	1.10	1.10	1.07	1.09	1.06	1.07
In-gas analysis:									
Olefins	0.17	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20
O_2	5.8	5.9	5.9	5.8	5.8	5.8	5.8	5.8	5.8
CH_4	84.9	84.6	84.6	84.6	84.7	84.8	84.7	84.7	84.6
Off-gas analysis:									
CO_2	2.0	1.7	1.7	1.9	2.2	2.5	1.6	1.4	1.5
Olefins	0.0	0.05	0.1	0.05	0.05	0.05	0.05	0.07	0.05
O_2	0.2	0.25	0.3	0.3	0.3	0.3	0.3	0.25	0.3
H_2	0.65	2.2	2.4	3.0	2.6	3.0	1.7	1.6	1.7
CO	0.55	0.8	0.9	0.8	0.6	0.5	0.8	0.8	0.9
C_2H_6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CH_4	89.2	87.1	86.7	87.1	87.1	86.9	87.3	87.8	87.0
$\frac{\text{Volume in-gas}}{\text{Volume off-gas}}$	1.08	1.07	1.05	1.06	1.06	1.06	1.07	1.08	1.07
Condensate, gm./100 litres in-gas at N.T.P.									
Total	5.52	5.21	5.12	4.65	4.31	3.77	6.30	6.00	6.11
CH_3OH	1.01	0.96	0.90	0.70	0.57	0.06	1.54	1.55	1.49
CH_2O	0.032	0.043	0.037	0.009	0.013	0.009	0.018	0.017	0.018
HCOOH	0.036	0.036	0.029	0.032	0.031	0.003	0.043	0.042	0.040
H_2O	4.44	4.16	4.16	3.91	3.70	3.70	4.70	4.40	4.56
Alcohol in condensate, %	18.3	18.5	17.5	15.1	13.2	1.67	24.3	25.8	24.5
Total carbon oxidized, %	3.68	3.62	3.69	3.59	3.59	3.39	3.94	3.72	3.92
Yields as % of total carbon burned to:									
CH_3OH	22.5	22.0	20.0	16.1	13.0	1.53	32.1	34.3	31.4
CH_2O	0.76	1.05	0.88	0.23	0.32	0.24	0.40	0.41	0.40
HCOOH	0.56	0.57	0.45	0.51	0.50	0.43	0.64	0.65	0.59
Total	23.82	23.62	21.33	16.84	13.82	2.20	33.14	35.36	32.39
Total inlet oxygen accounted for, %	94	90	89	89	89	90	97	90	94

as good a catalyst as copper. However, in both of these previous investigations the form of the silver catalyst was not the same as the form of the copper catalyst with which it was compared. In view of the fact that the physical character of the catalyst appears to be important, the comparison of silver and copper in the previous investigations was probably not justified.

The low yields produced by the zinc gauze in Experiments 14 to 16 are not unexpected since reversible oxidation–reduction of zinc does not occur under

TABLE III

EXPERIMENTS WITH NICKEL IN THE FORM OF BLOCKS

Experiment No.	20	21	22	23	24	25	26
Temperature, ° C.	450	450	450	450	450	450	450
Pressure, atm.	185	188	182	181	185	179	181
Off-gas flow, litres/min.	1.07	1.07	1.09	1.10	1.09	1.18	1.07
In-gas analysis:							
Olefins	0.20	0.20	0.20	0.20	0.20	0.15	0.15
O_2	5.8	5.8	6.0	6.0	5.8	6.0	5.9
CH_4	84.6	84.7	84.0	85.0	85.1	84.4	84.6
Off-gas analysis:							
CO_2	1.15	1.3	1.5	1.7	1.7	1.1	1.15
Olefins	0.05	0.05	0.05	0.05	0.05	0.05	0.05
O_2	0.3	0.3	0.3	0.3	0.35	0.25	0.35
H_2	1.5	1.4	2.0	2.5	1.35	1.55	1.95
CO	1.2	1.1	0.90	0.80	0.60	1.25	0.90
C_2H_6	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CH_4	87.5	87.6	87.2	86.7	87.4	86.7	87.4
$\frac{\text{Volume in-gas}}{\text{Volume off-gas}}$	1.07	1.07	1.07	1.06	1.06	1.07	1.07
Condensate, gm./100 litres in-gas at N.T.P.							
Total	7.28	6.79	6.43	5.40	6.12	7.54	6.24
CH_3OH	1.76	1.70	1.49	1.36	1.42	1.76	1.41
CH_2O	0.062	0.053	0.032	0.036	0.027	0.056	0.032
HCOOH	0.033	0.030	0.029	0.033	0.028	0.027	0.030
H_2O	5.43	5.02	4.93	3.97	4.65	5.69	4.77
Alcohol in condensate, %	24.1	25.0	23.2	25.1	23.2	23.4	22.5
Total carbon oxidized, %	4.09	4.09	3.92	3.93	3.73	4.17	3.52
Yields as % of total carbon burned to:							
CH_3OH	35.3	34.1	31.6	28.3	31.1	34.9	32.9
CH_2O	1.34	1.14	0.68	0.79	0.64	1.19	0.80
HCOOH	0.46	0.42	0.43	0.47	0.42	0.37	0.48
Total	37.10	35.66	32.71	29.56	32.16	36.46	34.18
Total inlet oxygen accounted for, %	93	99	95	87	97	100	91

the conditions of these experiments and, consequently, the mechanism proposed for the production of methanol is not possible. These three experiments were made in sequence and it is suggested that during the first two experiments the oxidation of zinc was not complete but that late in the second experiment, or early in the third, the zinc had become completely oxidized and inactive, and hence almost no methanol was obtained in the third experiment.

Experiments 17, 18, and 19 offer a comparison of nickel, in the form of gauze, with the other catalysts. The yield of methanol is slightly higher than for copper gauze (Experiments 6 to 10) and appeared to be worth further study.

Catalysts should be compared under optimum conditions, differences in the behavior being most marked under the most favorable conditions; under unfavorable conditions all the catalysts may be expected to approach the same inefficient state. The results presented in Table I showed that gauze is not the best form of catalyst, at least for copper, and indicated that a comparison of the activities of various metals in the form of gauze should be considered only as a preliminary screening. Therefore, a series of tests was made with nickel in the form of blocks; the results are shown in Table III.

Comparing the two forms of each of the two catalysts, copper and nickel, the order of effectiveness is copper blocks (Table I), nickel blocks (Table III),

TABLE IV

EXPERIMENTS USING MONEL METAL

Experiment No.	27	28	29	30
Temperature, ° C.	450	450	450	450
Pressure, atm.	180	181	182	177
Off-gas flow, litres/min.	1.08	1.08	1.09	1.11
In-gas analysis:				
Olefins	0.15	0.17	0.15	0.15
O_2	5.8	6.0	6.1	6.1
CH_4	84.5	84.8	84.3	84.5
Off-gas analysis:				
CO_2	1.04	1.69	1.05	1.13
Olefins	0.05	0.05	0.05	0.05
O_2	0.35	0.45	0.35	0.35
H_2	1.55	1.7	1.95	2.08
CO	0.95	0.5	1.0	1.0
C_2H_6	0.0	0.0	0.0	0.0
CH_4	87.7	86.5	87.1	86.7
$\frac{\text{Volume in-gas}}{\text{Volume off-gas}}$	1.07	1.05	1.07	1.06
Condensate, gm./100 litres in-gas at N.T.P.				
Total	6.68	5.83	7.00	6.92
CH_3OH	1.57	0.98	1.58	1.57
CH_2O	0.027	0.017	0.032	0.033
HCOOH	0.031	0.024	0.035	0.025
H_2O	5.05	4.80	5.35	5.30
Alcohol in condensate, %	23.5	16.9	22.6	22.6
Total carbon oxidized, %	3.54	3.30	3.61	3.67
Yield as % of total carbon burned to:				
CH_3OH	36.7	24.5	36.2	35.3
CH_2O	0.67	0.46	0.78	0.80
HCOOH	0.50	0.42	0.56	0.39
Total	37.87	25.38	37.54	36.49
Total inlet oxygen accounted for, %	94	94	93	94

nickel gauze (Table II), and copper gauze (Table I). The two gauze catalysts gave very similar yields, suggesting that the form of the catalyst was the predominating influence in this case. When it is considered that the conditions of all of these experiments are those that have been determined to be the optimum for copper, nickel appears to offer some promise. It is possible that when the optimum conditions for the nickel catalyst have been determined it may show considerable superiority over copper.

It was also considered that the possible existence of a promoter effect might endow an alloy of copper and nickel with greater activity than is possessed by either metal alone. A series of experiments was therefore carried out using a catalyst of $\frac{1}{4}$ in. lengths of Monel metal wire 0.08 in. diameter. The results of Experiments 27 to 30 (Table (IV)) appear to demonstrate that Monel metal has catalytic properties quite similar to those of nickel. It may be somewhat superior to nickel, and in any case it also appears to be worthy of further study.

It is proposed that further experiments should now be carried out with both nickel and Monel metal. A systematic investigation of the effect of the variables, temperature, pressure, composition, and rate of flow is proposed, using sulphur-free gas, to determine the maximum conversion to methanol that can be obtained with these catalysts under the optimum conditions for each. It is expected that a considerable improvement in the conversion to methanol can be obtained by improving the conditions, following which consideration can be given to the advisability of investigating a recirculatory process.

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THE HETEROGENEITY OF ACTIVATED COCOANUT-SHELL CHARCOAL[1]

C. C. Coffin[2] and B. F. Long[3]

Abstract

The individual adsorption capacities of over 500 granules of 6 to 10 mesh activated cocoanut-shell charcoal were determined by weighing each piece separately on a microbalance before and after saturation with carbon tetrachloride vapor. The particle capacities were found to be distributed over a probability curve represented by the equation

$$y = 14.6\, e^{-0.0036x^2}\,.$$

Small particles adsorb more carbon tetrachloride than large ones and dense particles more than those of lesser density.

Introduction

In the course of some work on the testing of activated cocoanut-shell charcoals for respirators, it was found that the observed activities seemed to depend on the method of sampling. This suggested that the material was heterogeneous in the sense that some particles were more adsorbent than others. In most of the work that has been done on such charcoals, relatively large samples containing many granules have been used. It is thus possible that significant differences in particle activity have been overlooked. This paper describes experiments designed to explore the extent and nature of any such heterogeneity. Attention is confined to the adsorption capacity (weight activity) of the dry charcoal.

Experimental

The individual adsorption capacities of the charcoal particles were determined by weighing each piece separately on a microbalance before and after saturation with carbon tetrachloride vapor. The torsion microbalance was adapted from that described in a paper by Fabergé (1). A sketch of its working parts is shown in Fig. 1. It was constructed from 'Meccano' parts firmly mounted in a strong wooden box. The torsion spring, T, consists of 104 turns (2 mm. in diam.) of 0.004 in. spring-tempered phosphor bronze wire. The ends of the spring are clamped in small brass chucks connected to the shafts, S and S', by standard Meccano couplings. The light glass beam, which is cemented to the middle of the helical spring, passes through a 2 by 1 mm. window in the side of the balance case into another closed chamber (a chalk box) provided with an easily operated and tightly fitting door of transparent plastic. The balance pan, P, is made of light aluminium foil and is

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Contribution from the Department of Chemistry, Dalhousie University, Halifax, N.S.

[2] *Shirreff Professor of Chemical Research.*

[3] *At the time, Graduate Student in Chemistry. Present address: Memorial College, St. John's, Newfoundland.*

hung from the beam in this outer chamber in which an atmosphere of dry air or a partial pressure of carbon tetrachloride can be maintained. The end of the glass beam is drawn out into a fine point which, by moving the index, *I*, may be aligned with a similar fixed point and viewed through a lens system against an illuminated ground-glass background from the front of the balance. The adjustable pointer-index, *I*, is carried by the shaft, *S*, so that, by turning it counterclockwise, the spring may be wound up to offset the effect of a weight added to the pan. The dial is a 14 in. varnished cardboard protractor divided into 0.25 degrees of arc and mounted on a 'Masonite' panel. The sensitivity of the balance is 15.85° of arc per mgm. or 0.000016 gm. per scale division.

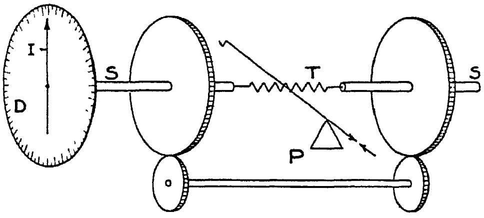

FIG. 1. *Working parts of microbalance.*

The geared construction does not limit the pointer movement to something less than 360° as is the case with Fabergé's instrument. It can be 'wound up' indefinitely. The calibration curve is strictly linear over the range used (5 to 25 mgm.) in the charcoal weighings. There is a hysteresis effect in that the zero point tends to drift slightly under load and return when the balance is at rest. This drift was checked and corrected for by determining the zero point after every fifth weighing. The balance is well damped and protected from drafts, and weighings can be made rapidly enough to avoid errors due to loss of carbon tetrachloride or pick-up of water vapor. By varying the length and diameter of wire and helix, a balance having practically any desired sensitivity can be very easily constructed.

To handle the individual pieces of charcoal, and to be able to identify them throughout a series of weighings, the following procedure was adopted. Arrays of narrow deep depressions in numbered rows and columns were stamped in square sheets of wire gauze to serve as receptacles for the charcoal pieces. Each gauze served as a tray that could be placed in oven (130°), desiccator, or carbon tetrachloride chamber. To carry out a series of measurements a piece of charcoal picked at random from a sample dried to constant weight was placed in each depression of a tray which was immediately put in a chamber at room temperature containing air saturated with carbon tetrachloride vapor. After coming to equilibrium, the particles were weighed as rapidly as possible and returned to their respective positions on the tray, which was then placed in the oven. After the carbon tetrachloride had been removed (16 hr. at 130° C.) the tray was placed in a shallow desiccator, the particles were weighed again, and the adsorption capacity of each piece was calculated. A shallow dish of carbon tetrachloride was placed in the balance case during the first weighings and calcium chloride during the second. No difficulty due to loss of carbon tetrachloride or gain of water vapor was experienced in obtaining a balance point. Two operators are necessary however—one to load and unload the pan, the other to balance it and record the weights.

All experiments described here were made with a sample (SBT 95-96) of charcoal obtained from the National Research Council. In order to eliminate any extreme differences in particle capacity that might be associated with very large or very small particles, and in order to bring the pieces to be weighed into a workable range on the balance, the sample was screened (unless otherwise stated). The fraction that passed a 6 mesh and was retained by a 10 mesh screen was used for the measurements of individual adsorption capacity.

Results

The results obtained for 480 pieces of this 6 to 10 mesh charcoal are given in Table I and are plotted as a distribution histogram in Fig. 2. The amounts of carbon tetrachloride taken up are tabulated and plotted in groups differing by 5% based on the charcoal dry weight. That is, the increment of the

TABLE I

DISTRIBUTION OF INDIVIDUAL ADSORPTION CAPACITIES

% CCl_4 adsorbed, (gm./100 gm. charcoal)	No. of pieces, (total = 480)	% of total No.
2	2	0.4
7	4	0.8
12	10	2.1
17	5	1.0
22	16	3.3
27	23	4.8
32	31	6.5
37	51	10.1
42	73	15.0
47	68	14.1
52	53	11.0
57	49	10.0
62	23	4.8
67	23	4.8
72	17	3.5
77	6	1.2
82	11	2.3
87	5	1.0
92	5	1.0
97	2	0.4
102	3	0.6

abscissa in the figure, and of Column 1 in the table, is 5%. Thus, the ordinate at 27% adsorption, for example, gives the percentage of particles (Column 3) adsorbing between 25 and 29% inclusive of their dry weight of carbon tetrachloride. The curve in the figure is the Gauss 'error' curve having an equation of the form

$$y = k\,e^{-h^2x^2},$$

in which y is the ordinate of a point, k is a constant equal to the ordinate where $x = 0$, x is the positive or negative variation from this central ordinate, and h is a constant. In the figure the constants ($k = 14.6$, $h = 0.06$) have been roughly fitted to the data in order to show that the type of heterogeneity found is that which might have been predicted for such a granular and randomly mixed material. The point at which $x = 0$ has been taken as 47%.

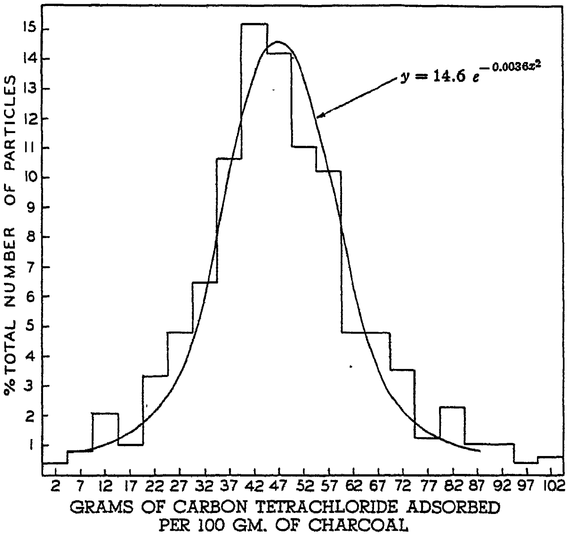

FIG. 2. *Distribution of charcoal activity.*

The reproducibility of the method was tested by repeating the whole procedure with one lot (29 pieces) of charcoal. The results are shown in Table II. With few exceptions the two adsorptions agreed as closely as can be expected in work of this kind.

Charcoal Fractionation

The possibility of using some physical property to separate the charcoal into fractions of high and low adsorption capacity was investigated. It was found that the smaller particles had a greater adsorption capacity and heat of wetting than the larger, and that the denser pieces had greater capacities than the less dense.

Figs. 3*A* and 3*B* show the distribution of adsorption capacity among manually separated large and small particles of 6 to 10 mesh charcoal. Table III gives the relative heats of wetting (as temperature change per gram of charcoal) in benzene of eight different 2 gm. batches of hand-separated large and small pieces. It is evident that the smaller particles are more adsorbent than the larger.

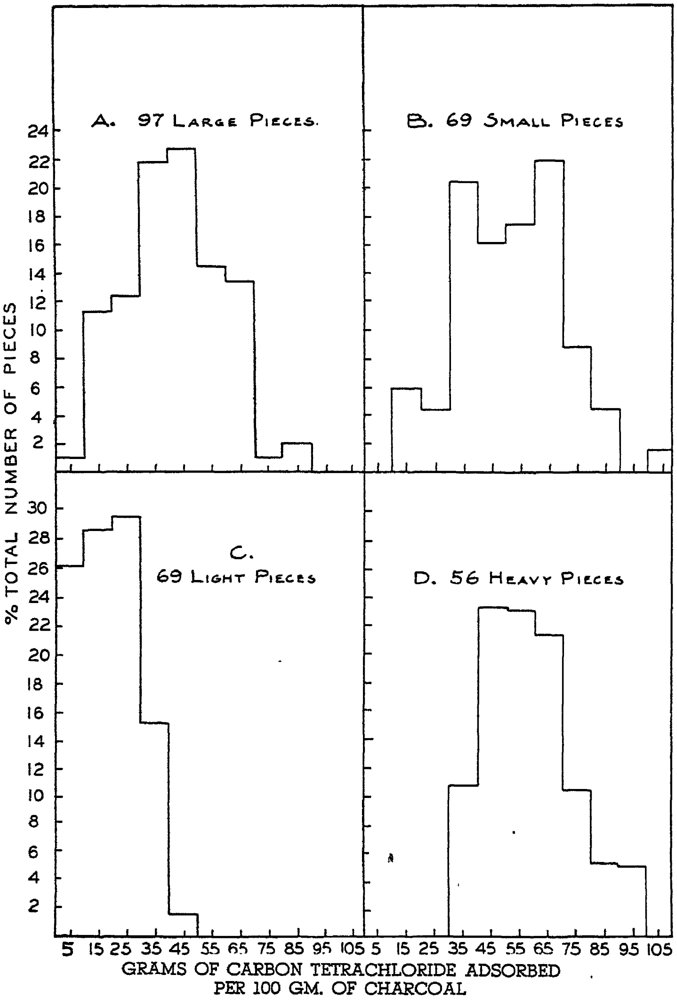

FIG. 3. *Variation of charcoal capacity with size and density of particles.*

A more clean-cut separation of the charcoal into fractions of high and low adsorption capacity was achieved by fractional flotation in a liquid mixture. A dried 6 to 10 mesh sample was boiled in carbon tetrachloride to expel air. After cooling to room temperature the carbon tetrachloride (sp. gr., 1.6) and charcoal was stirred and slowly diluted with ethylene dibromide (sp. gr., 2.18) until about half the charcoal floated (sp. gr. liquid, 1.85). The two charcoal fractions were then separated and, after removal of the carbon tetrachloride and ethylene dibromide, were investigated piece by piece on the microbalance.

TABLE II

RESULTS OF REPEATED DETERMINATION OF INDIVIDUAL ADSORPTION CAPACITY

Weights in milligrams

Weight dry piece		Weight saturated piece		Weight CCl_4 adsorbed		% Diff. CCl_4 weights
First	Second	First	Second	First	Second	
5.22	5.17	8.80	8.71	3.58	3.54	1.1
9.98	9.86	14.93	15.02	4.95	5.16	4.1
6.13	6.10	8.66	8.73	2.53	2.63	3.8
3.86	3.88	7.04	7.15	3.18	3.27	2.7
2.46	2.43	4.10	4.18	1.64	1.75	6.3
9.57	9.52	12.43	12.57	2.86	3.05	6.3
6.32	6.33	9.02	9.11	2.70	2.78	2.9
9.33	9.27	11.38	11.52	2.05	2.27	9.7
9.68	9.55	13.79	13.77	4.11	4.22	2.6
8.42	8.43	11.83	11.84	3.41	3.41	0
6.30	6.28	6.68	6.74	0.38	0.46	17.4
9.14	9.15	13.63	13.70	4.49	4.55	1.3
4.72	4.69	6.64	6.68	1.92	1.99	3.5
2.29	2.27	3.68	3.70	1.39	1.43	2.8
3.97	3.93	5.25	5.30	1.28	1.37	6.6
9.25	9.21	13.57	13.60	4.32	4.39	1.6
2.37	2.35	4.09	4.22	1.72	1.87	8.0
10.93	10.35	15.10	15.19	4.17	4.84	13.8
4.42	4.40	6.60	6.63	2.18	2.23	2.2
4.08	4.07	7.18	7.22	3.10	3.15	1.6
5.98	6.03	9.01	9.08	3.03	3.05	0.7
2.18	2.17	3.37	3.67	1.19	1.50	20.0
2.00	1.99	3.63	3.60	1.63	1.61	1.2
4.17	4.17	5.47	5.45	1.30	1.28	1.6
5.65	5.67	8.29	8.44	2.64	2.77	4.7
13.48	13.50	16.75	17.00	3.27	3.50	6.6
8.26	8.29	12.85	12.77	4.59	4.48	2.5
7.46	7.49	11.68	11.60	4.22	4.11	2.7
10.78	10.82	16.13	16.04	5.35	5.12	4.5

TABLE III

TEMPERATURE RISE IN BENZENE (20 CC. BENZENE; 2 GM. CHARCOAL; 20° C.)

Large pieces, ° C. per gm. charcoal	Small pieces, C. per gm. charcoal
2.07	2.65
2.02	2.44
2.13	2.38
2.05	2.44

The distribution of particle adsorption capacities in the light and heavy fractions is shown in Figs. 3*C* and 3*D*. It is evident that a remarkably sharp separation has taken place. This fractionation can be continued and small samples of very good and very poor charcoal may be readily obtained.

The writers are not aware of any previous work on this charcoal heterogeneity, and are not prepared to discuss why some granules should be so much better than others. The fact that small dense pieces are better than larger and lighter ones would seem, however, to point to differences existing among the cocoanut shells themselves rather than to 'ups and downs' in whatever activating process they have undergone. Preliminary work has indicated that the best pieces of cocoanut charcoal are better than the best pieces of several synthetic charcoals, which, as might be expected, seem to be more uniform than the 'natural' variety.

A possibility that suggests itself here is the use of the probability equation, $y = k\, e^{-h^2x^2}$, to describe charcoals or granular adsorbents in general. Each specimen would be characterized by two constants, h and k, indicating its over-all adsorption capacity and the spread of the capacities of the individual particles.

Reference

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STUDIES IN THE FORMATION OF DDT[1]

By T. A. Eastwood,[2] D. L. Garmaise,[3] D. J. Morantz,[4] and C. A. Winkler[5]

Abstract

In the condensation of chloral and chlorobenzene in sulphuric acid to yield DDT, the yield of DDT is increased and the rate of formation of DDT decreased by (1) decreased sulphuric acid concentration, (2) decreased molar amount of sulphuric acid, and (3) lowered temperatures. Reversible sulphonation of chlorobenzene is the major side reaction; the presence of 4-chlorobenzenesulphonic acid reduces the extent of this reaction. Increased yields (based on chloral) can be obtained by using excess chlorobenzene. A mechanism is proposed involving 1-(4-chlorophenyl)-2,2,2-trichloroethanol, which has been isolated from the reaction, and 1-(4-chlorophenyl)-2,2,2-tricholorethyl bisulphate, whose barium salt reacts with chlorobenzene in sulphuric acid to give DDT.

Introduction

The general reaction involving the condensation of two moles of an aromatic compound with one mole of an aldehyde to form a 1,1-diaryl alkane was first studied by Baeyer in 1872 (1) and has come to be known as the Baeyer condensation. It has recently been found that 1,1-di(4-chlorophenyl)-2,2,2-trichloroethane (*p,p′*-DDT), a product of this type of reaction first prepared by Zeidler (14), is a powerful contact insecticide (10).

In their research on the Baeyer condensation of chloral and benzene with sulphuric acid, Chattaway and Muir (4) were able to isolate 1-phenyl-2,2,2-trichloroethanol. Since this compound will react with one mole of benzene to give the normal Baeyer condensation product, they believe that this alcohol is a precursor of the usual Baeyer product. Previously, Dinesmann (6) had isolated the same alcohol using aluminium chloride catalyst, although neither he nor Frankforter and Kritchevsky (7) (who repeated Dinesmann's procedure) appear to have considered its intermediary nature. Rueggeberg *et al.* (12, 13) have reported the use of chlorosulphonic acid as the condensing agent and have postulated a mechanism for the reaction involving the alcohol as an intermediate. Mosher *et al.* (11) have reported their work on the preparation of technical DDT. Although their experimental techniques differ from those used in the present study, the conclusions they reach concerning the effect of the reaction variables are in qualitative agreement with those presented here.

The present study was initiated to determine the optimum conditions for the production of *p,p′*-DDT using sulphuric acid catalysis, and to investigate the mechanism of the reaction.

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Contribution from the Physical Chemistry Laboratory, McGill University, Montreal, Que., with financial assistance from the National Research Council of Canada.

[2] *Graduate student and holder of a Canadian Industries Ltd. Fellowship. At present: Chemist, Chalk River Laboratories, National Research Council.*

[3] *Graduate student and holder of a Fellowship under the National Research Council of Canada. At present: Assistant Professor, Department of Chemistry, University of New Brunswick, Fredericton, N.B.*

[4] *Graduate student and holder of a Bursary under the National Research Council of Canada.*

[5] *Professor of Chemistry.*

Experimental and Results

Materials

Chloral hydrate, Eastman's white label grade, was recrystallized once from chloroform.

Chloral, obtained by the dehydration of chloral hydrate with sulphuric acid, was purified by distillation. The product so obtained gave a negligible precipitate of aluminium hydroxide when refluxed with a toluene solution of aluminium isopropoxide, hence it was considered sufficiently anhydrous for the present purpose.

Chlorobenzene, Eastman's yellow label grade, was distilled and the fraction boiling between 131° and 132° C. was used.

Sulphuric acid, Baker's C.P. grade, was suitably diluted with distilled water, or fortified with Mallinckrodt's fuming sulphuric acid (25% SO_3) to give the desired strength. It was analyzed by titration with standard sodium hydroxide solution, which in turn was standardized with potassium hydrogen phthalate.

1-(4-Chlorophenyl)-2,2,2-trichloroethanol was synthesized by a method suggested by Barry (2). 4-Chloroacetophenone, formed from chlorobenzene and acetic anhydride with aluminium chloride catalysis, was photochemically chlorinated at 200° to 210° C. and the 1-(4-chlorophenyl)-2,2,2-trichloroethanone formed was reduced to the alcohol using aluminium isopropoxide. The white crystalline product melted at 47° to 47.5° C. (corr.) after several recrystallizations. It was further characterized by conversion to the acetate by Howard's method (9). The yield was 90% of the theoretical, the melting point of the product being 123° to 124° C. (corr.) (Howard reports 121° to 122° C.).

4-Chlorobenzenesulphonic acid was prepared according to the directions of Baxter and Chattaway (3). After one recrystallization from water it analyzed 94% pure and melted between 90° and 95° C.

Experimental Procedure

The desired amount of chloral hydrate was weighed (or if chloral itself, was measured from a microburette) into a tared 50 ml. wide-mouthed Erlenmeyer flask and the sulphuric acid added from a 50 ml. burette. The acid concentrations in the treatment which follows have been corrected for the dilution of the acid by the water content of the chloral hydrate. The chlorobenzene was then added to the reaction mixture as rapidly as possible from a 10 ml. burette. The flasks were clamped in a thermostat regulated within 0.1° C., each mixture being agitated by means of a glass stirrer of the centrifugal type, driven at about 600 r.p.m. from a countershaft. With certain mole ratios of reactants this type of stirring did not adequately agitate the dense DDT slurry produced; therefore in these experiments a $\frac{1}{2}$ by 5 in. test tube replaced the usual 50 ml. reaction flask, and a closely fitting, flat twisted glass blade impeller was used.

The reaction was assumed to start when stirring was begun in the heterogeneous reaction mixture, and was quenched by diluting the sulphuric acid with about 20 gm. of chopped ice. About 15 ml. of chloroform was then added to the mixture to dissolve the organic material, and the acid layer carefully separated. The chloroform solution was then washed free of acid with distilled water, after which the chloroform and the small amount of water remaining were removed by distillation on a steam bath followed by heating for two hours at 50° C. at 1 mm. of mercury pressure. The net increase in weight was taken as crude DDT.

The *p,p'*-DDT content of the crude product was estimated by quantitative recrystallization from ethanol previously saturated with *p,p'*-DDT at 0° C. The procedure was adapted from that of the Chemical Inspection Department of the British Ministry of Supply as suggested by Messrs. Geigy (5). For each gram of crude product obtained, 10 ml. of solvent was added, and the solid was dissolved by heating the mixture under reflux. The *p,p'*-DDT was allowed to crystallize out by cooling the flask at room temperature for one hour and adding seeds if necessary. The crystallization process was continued at 0° C. for four hours. The precipitated material was filtered on a tared sintered glass crucible, washed twice with 10 ml. of cold 95% ethanol saturated with *p,p'*-DDT, dried to constant weight at 80° C., and weighed. For purposes of calculation the recrystallized material was assumed to represent all the *p,p'*-DDT in the sample.

The magnitude of the error involved in this method was estimated by analysis of synthetic mixtures of *p,p'*-DDT and *o,p'*-DDT. The main error is introduced by washing the chloroform solution with water, the accuracy of the entire procedure being about 5%. This was considered adequate in view of the nature of the reaction as a whole.

Stirring Speed and Rate of Reaction

Since the reaction is heterogeneous and the reactants form two layers, the effect of stirring speed was investigated. Two experiments were made using chloral, chlorobenzene, and sulphuric acid (97.4%) in a molar ratio of 1: 2: 20 at 30° C., one at stirring speed of 600 r.p.m. and the other at 1100 r.p.m. Since the rate of production was identical at both stirring speeds, subsequent experiments were made with a stirring speed of 600 r.p.m.

FACTORS AFFECTING THE YIELD OF DDT AND THE REACTION RATE

The effect of varying the acid concentration on the yield of DDT was investigated under widely different conditions of temperature and molar ratio of reactants, and by graphical interpolation of these data the yields of crude DDT for given acid concentrations and amounts shown in Table I were obtained. Since the general shape of the yield – acid concentration or

TABLE I

EFFECT OF ACID CONCENTRATION AND AMOUNT ON THE YIELD OF CRUDE DDT AND TIME FOR COMPLETE REACTION

Acid concentration, %	Yield of crude DDT and reaction time with molar ratios of:													
	1 : 2 : 2		1 : 2 : 3		1 : 2 : 5		1 : 2 : 10		1 : 2 : 20		1 : 2 : 40		1 : 2 : 80	
	%	Hr.	%	Hr.	%	Hr.	%	Hr.	%	Hr.	%	Hr.	%	Hr.
0° C.														
97									73.5	21				
98									84.5	13				
99									82.3	8				
101									58.9	2				
30° C.														
93									77.1	120	66.5	36		
94									77.7	30	69.0	19		
95									77.8	14	70.0	9	60.4	3
96					69.7	68			76.0	7	68.0	4	58.4	3
97					80.5	42			73.8	3	63.0	2	55.8	2
98			77.0	190+	84.0	24			70.0	1	54.5	1		
99			83.2	140	81.8	13			64.0	½	42.5	¼		
100			82.5	55	77.5	8			55.0	¼	26.5	<¼		
101			73.6	25	70.6	4			41.5	<¼				
102			63.1	10	64.0	2			20.0	<¼				
50° C.														
94					67.0	83	62.9	16						
96			60.0	70	71.9	27	67.5	6	60.4	2				
98			69.0	36	70.5	12	63.5	2	55.0	1				
100			73.0	24	65.3	5	50.0	½	39.9	¼				
101	63.1	72+	72.7	21	61.7	3	39.0	¼	26.5	<¼				
102	63.5	72+	70.0	19					15.9	<¼				
70° C.														
Maximum yield of p,p'-DDT														
94			15.0	18	21.0	10	23.2	5						
96			24.4	15	22.2	5	21.6	2						
98			25.8	12	22.8	3	19.9	½						
100	23.5	15	26.0	10	23.0	1	16.7	¼						

yield – acid amount curves is not affected by temperature over the range studied, only the values at 50° C., which are typical, are shown in Fig. 1 (where the experimentally observed values are also plotted) and Fig. 2.

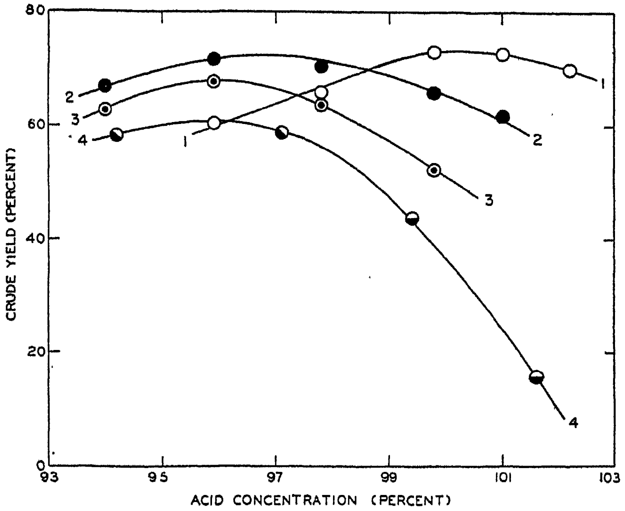


FIG. 1. *Effect of acid concentration on yield of crude DDT at 50° C. with chloral, chlorobenzene, and sulphuric acid in a molar ratio of 1 : 2 : 3—1; 1 : 2 : 5—2; 1 : 2 : 10—3; 1 : 2 : 20—4.*

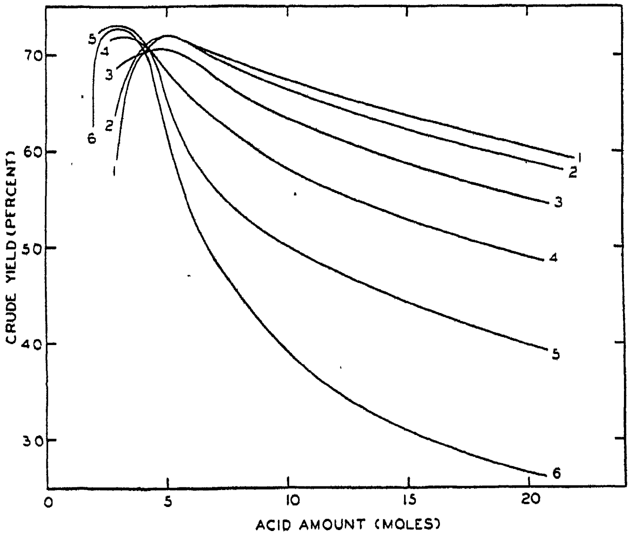


FIG. 2. *Effect of acid amount on yield of crude DDT at 50° C. with acid concentration of 96%—1; 97%—2; 98%—3; 99%—4; 100%—5; and 101%—6.*

Effect of Reactant Amounts

Experiments were made at 30° C. using other than the stoichiometric amounts of chlorobenzene, with the molar ratio of chloral to sulphuric acid maintained at 1 : 20. The rate data are plotted in Fig. 3.

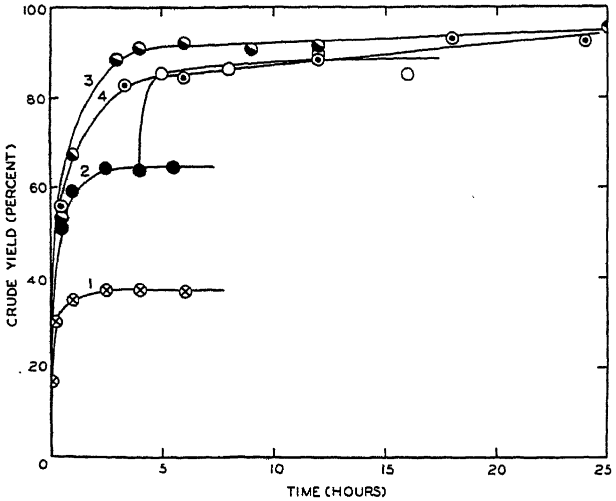


FIG. 3. *DDT formation with varying amounts of chlorobenzene at 30° C. Chloral, chlorobenzene, and sulphuric acid in molar ratio of 1 : 1 : 20—1; 1 : 2 : 20—2; 1 : 4 : 20—3; 1 : 6 : 20—4.*

Similar experiments were made with varying chloral amounts while the chlorobenzene – sulphuric acid ratio was 2 : 20. The results (Table II) indicate that, as compared with chlorobenzene, the chloral has little effect on the yield of *p,p'*-DDT.

When excess chlorobenzene was added to a normal reaction after the final yield of DDT had been reached, it was found that additional DDT was produced. For example, if two moles of chlorobenzene be added to a normal reaction at the end of four hours the yield was increased from 64 to 89% (Fig. 3).

Similar results were observed when additional sulphuric acid was added to a normal reaction using small amounts of acid. Using chloral, chlorobenzene, and sulphuric acid (101.9%) in a molar ratio of 1 : 2 : 3 for example, a yield of 64.4% was achieved in four hours and did not appreciably increase thereafter. But if an additional 17 moles of acid (94.8%) be added at the end of this period the yield is increased to 74%, which is as great as if 20 moles of sulphuric acid (94.8%) had been present initially. Presumably the catalytic action of the sulphuric acid had been inhibited by its dilution with the water formed from the DDT reaction and the sulphonation of chlorobenzene.

These results indicate that chloral or some compound intermediate between chloral and DDT is more stable in concentrated sulphuric acid than is chlorobenzene, and that the low yields obtained when the stoichiometric amount of chlorobenzene is employed are due to a side reaction involving chlorobenzene. Since 4-chlorobenzenesulphonic acid has been isolated from the acid layer at the end of a DDT reaction, and in view of the work of Mosher *et al.* (11), there can be little doubt that a major side reaction involved is the sulphonation of chlorobenzene.

TABLE II

DDT FORMATION WITH VARYING AMOUNTS OF CHLORAL AT 30° C.

Chloral, moles	Chlorobenzene, moles	Sulphuric acid (98.5%), moles	Time, hr.	*p,p′*-DDT yield, gm.	*p,p′*-DDT yield, %
0.0095	0.0191	0.191	0.25	0.68	20.0
0.01	0.02	0.20	0.50	1.16	32.8
			1.0	1.32	37.3
(Molar ratio 1 : 2 : 20)			2.0	1.40	39.3
			2.5	1.50	42.3
			4.0	1.59	45.0
			4.0	1.47	41.5
0.0191	0.0191	0.191	0.266	1.15	34.2
0.02	0.02	0.20	0.5	1.72	48.6
			1.0	1.73	48.9
(Molar ratio 2 : 2 : 20)			2.5	1.78	50.1
			4.0	1.87	52.7
0.0382	0.0191	0.191	0.25	0.90	26.9
0.04	0.02	0.20	0.5	1.79	50.5
			2.5	1.85	52.4
(Molar ratio 4 : 2 : 20)			4.0	1.89	53.4
			5.0	1.90	53.6
0.0572	0.0191	0.191	0.25	0.73	21.7
0.06	0.02	0.20	0.5	1.53	43.3
			3.0	1.60	45.5
(Molar ratio 6 : 2 : 20)			5.0	1.73	49.0

TABLE III

EFFECT OF ADDED 4-CHLOROBENZENESULPHONIC ACID ON DDT FORMATION

Chloral	0.01 mole (0.98 ml.)
Chlorobenzene	0.02 mole (2.04 ml.)
Sulphuric acid	0.20 mole (10.83 ml.)

Temperature, 30° C.

1	2	3	4	5	6
Added sulphonic acid, moles	Final crude yield, %	Final pure yield, %	Purity, %	Time for complete reaction, hr.	Concentration of H_2SO_4 allowing for sulphonic acid dilution, %
Nil	64.3	42.9	66.7	2.5	98.5
0.01	73.7	49.8	67.7	3.0	89.8
0.03	81.6	58.9	72.2	10.0	76.5
0.045	73.1	54.3	74.2	21.0	68.6
0.06	49.1	30.6	62.3	36.0	63.4

The shape of the yield – acid concentration or the yield – acid amount curves can then be explained on the basis of these two factors, the side reaction involving chlorobenzene, and the dilution of the catalyst. At low acid concentrations or amounts, the yields are low owing to the excessive dilution of the catalyst so that further reaction to form DDT is immeasurably slow. At higher concentrations or amounts this factor is not as important, and over a small range of concentrations the yield is maximal, representing optimum concentrations for a particular amount of acid at that temperature. If the acid concentration or amount is further increased, the sulphonation reaction becomes more prominent than the DDT reaction and the yield decreases because of the inadequate supply of chlorobenzene.

Since the sulphonation of chlorobenzene is a reversible reaction the presence of the product should favor increased chlorobenzene concentrations and hence DDT yields; the truth of this surmise is indicated by the data in Columns 1, 2, and 3 in Table III.

Factors Affecting Reaction Time and Rate

The effect on the time necessary for complete reaction of varying the amount of chloral and chlorobenzene is clear from Table II and Fig. 3; chloral has little effect but an increase in the amount of chlorobenzene results in a longer reaction time. This may be due to the greater dilution of the sulphuric acid by the water formed during the sulphonation of the chlorobenzene.

The minimum times required for the attainment of the final yield of DDT under different conditions of acid amount, concentration, and temperature have been given with the yields in Table I; those at 50° C. are typical in general outline and are shown in Fig. 4. Evidently an increase in acid amount while the concentration is constant, or an increase in the acid concentration while the amount is constant, results in shorter reaction times. Also, comparison of the results at different temperatures while the acid–reactant ratio is constant shows that an increase in reaction temperature results in a shorter reaction time, if the acid concentrations and amounts are fixed.

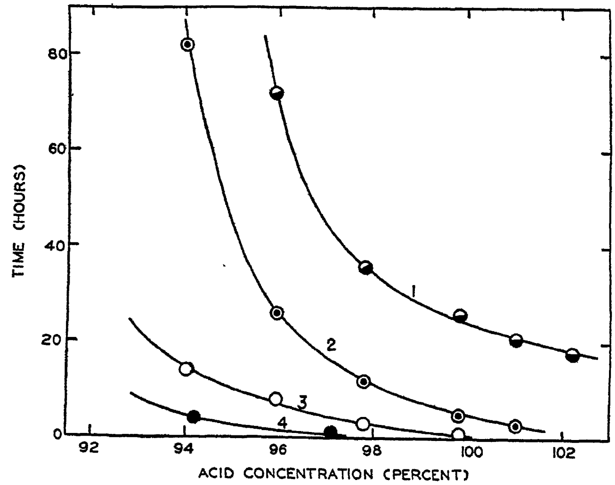


Fig. 4. *Effect of acid concentration on time for complete reaction at 50° C. with chloral, chlorobenzene, and sulphuric acid in molar ratio of 1 : 2 : 3—1; 1 : 2 : 5—2; 1 : 2 : 10—3; 1 : 2 : 20—4.*

These curves show the high order of dependence on acid concentration and amount of the time for complete reaction. The shape of the curve for a molar ratio of 1 : 2 : 5 at 50° C., for example, shows the impracticability of working with acid concentrations below 94% under these conditions.

Not only does the time for complete reaction vary with the amount and concentration of the acid employed, but the velocity of the reaction also depends on these factors. Figs. 5 and 6 show typical rate curves for the production of DDT. In Fig. 5 the acid amount is varied while the concentra-

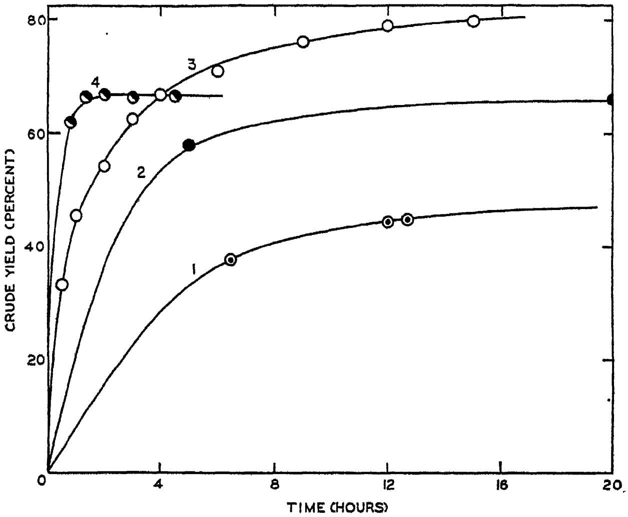


FIG. 5. *Effect of acid amount on rate at 30° C. with chloral, chlorobenzene, and sulphuric acid in molar ratio of 1 : 2 : 2—1; 1 : 2 : 3—2; 1 : 2 : 5—3; 1 : 2 : 10—4.*

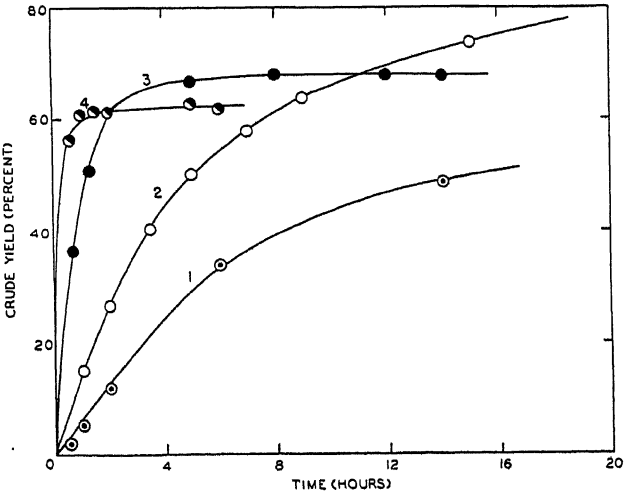


FIG. 6. *Effect of acid concentration on rate at 30° C. 93.1%—1; 94.3%—2; 98.3%—3; 99.4%—4.*

tion is constant, and in Fig. 6 the concentration is varied while the amount is constant. Since it is impossible to compare the rate curves using 93.1 and 99.4% or 2 and 10 moles of sulphuric acid on the same scale, only the early portions of the rate curves for low acid concentrations or amounts are shown graphically.

It is clear that an increase in acid concentration has the same qualitative effect as an increase in acid amount, namely, to increase the reaction rate.

Satisfactory specific rate constants for the reaction were not obtained, owing to the complexity of the main and side reaction, the experimental error, and the continual dilution of the sulphuric acid by the water eliminated in both the normal DDT reaction and the sulphonation of chlorobenzene. Initial rate measurements were also not sufficiently accurate to yield reliable rate constants.

PURITY OF THE CRUDE PRODUCT

The formation of DDT isomers is a side reaction of equal importance with the sulphonation of chlorobenzene. The proportion of *p,p'*-DDT in the crude product (% purity of the product) has been found to be constant throughout a reaction under given conditions. The careful analysis of a number of samples of crude DDT from commercial sources has shown that the major impurity in crude DDT is 1-(4-chlorophenyl)-1-(2-chlorophenyl)-2,2,2-trichloroethane (*o,p'*-DDT) and that all other impurities together constitute less than 5% of the crude, depending on the purity of the initial reactants (8).

The *p,p'*-DDT: *o,p'*-DDT ratio is increased by decreasing the temperature, as shown by the average of all the purity values at a given temperature listed in Table IV.

TABLE IV

EFFECT OF TEMPERATURE ON PURITY

Temperature, ° C.	Average purity, %
0	73.2
30	64.0
50	57.6
70	48.0

As shown by the values listed in Columns 1 and 4 of Table III the addition of 4-chlorobenzenesulphonic acid changes the ratio of the isomers. This may be because the 4-chlorobenzenesulphonic acid alters the reaction environment.

However, under three special conditions the purity of the product has not been found constant throughout the reaction.

(1). At 70° C. the purity decreases as the reaction time increases. The values given for the crude yield, *p,p'*-DDT yield, and purity of the crude product given in Table V are typical and indicate that some reaction is following the formation of DDT by which the *p,p*′-DDT is being converted to a water insoluble, but alcohol soluble compound. Since the yield of the crude increases, the product formed cannot be a degradation product of *p,p*′-DDT, but may be a complex formed by polymerization or by reaction with sulphuric acid. For this reason only the maximum *p,p*-′DDT yield has been entered in Table I at 70° C.

TABLE V

CHANGE IN *p,p*′-DDT CONTENT OF CRUDE PRODUCT WITH REACTION TIME AT 70° C.

Chloral	0.02 mole (1.96 ml.)
Chlorobenzene	0.04 mole (4.07 ml.)
Sulphuric acid (96.1%)	0.10 mole (5.55 ml.)

Molar ratio 1 : 2 : 5

Time, hr.	Crude yield as % DDT	*p,p*′-DDT yield, %	Purity, %
1.0	29.7	14.8	49.8
2.0	35.4	18.2	51.6
4.0	52.2	22.6	43.3
9.5	55.2	21.6	38.4
20.0	57.6	19.8	34.4
28.0	61.8	—	—
36.5	62.7	18.2	29.0

(2). When excess chloral is used under otherwise normal conditions, the purity of the product is low. The impurity may be 1-(4-chlorophenyl)-2,2,2-trichloroethanol, since Chattaway and Muir have used somewhat similar conditions (i.e., excess aldehyde) to prepare the analogous compound, 1-phenyl-2,2,2-trichloroethanol (4). Since this may contaminate the crude product, only the *p,p*′-DDT yield was considered when the effect of excess chloral on the reaction was discussed.

(3). At 0° C., when the acid concentration was below 98.5%, it was found that the purity increased gradually to the value 73.2% previously established as the purity at 0° C.

The amount of impurity appearing in the early portions of the reaction can be calculated since the *p,p*′-DDT:total DDT ratio has previously been established as 73.2% at 0° C. From this ratio the total DDT yield for a corresponding *p,p*′-DDT yield can be arrived at, and the difference between the crude yield and total DDT yield represents the amount of impurity. By this method the values plotted in Fig. 7 were obtained. Since the impurity follows the appearance–disappearance curve usually associated with a reaction occurring in consecutive steps with about the same rates, the isolation and characterization of this material was undertaken.

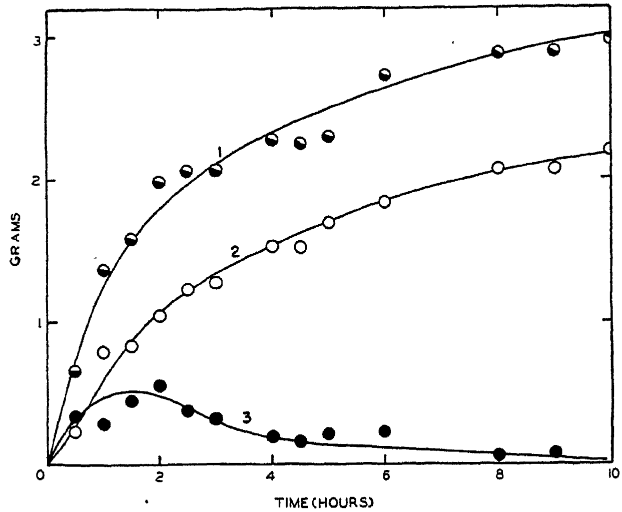


FIG. 7. *Rate of formation of crude DDT at 0° C.—1; p,p′-DDT—2, and intermediate alcohol—3.*

Isolation and Characterization of the Intermediate

The previous work of Chattaway and Muir (4) indicated that the probable intermediate in the DDT reaction was 1-(4-chlorophenyl)-2,2,2-trichloroethanol (which will be referred to as the alcohol), and therefore this compound was prepared for reference, as previously mentioned.

A sample of the substance indicated by the rate curves to be intermediate in the sulphuric acid condensation was obtained by duplicating on a large scale the procedure used in the rate studies, and distilling the product under reduced pressure. The yield obtained in this way agreed with that calculated indirectly from the rate studies. After fractional distillation under reduced pressure, a middle fraction was obtained which crystallized after three months and on recrystallization melted at 44° to 46° C. A mixture of this material with an authentic sample of the alcohol melted at 45.5° to 46° C. The material was further characterized by converting it to the acetate, and the product melted at 122.5° to 124° C., the melting point of a mixture of this product with a sample of the acetate being 122° to 124° C.

Thus it appears that the intermediate indicated by the rate data is 1-(4-chlorophenyl)-2,2,2-trichloroethanol, probably contaminated with the ortho-isomer, 1-(2-chlorophenyl)-2,2,2-trichloroethanol.

At 0° C. an increasing degree of purity was observed with acid concentrations of 98.5% or lower, while at 30° C. there was a slight indication of this type of behavior using chloral, chlorobenzene, and sulphuric acid in a molar ratio of 1 : 2 : 3 when the acid concentration was 95.9% or lower. No trace of intermediate accumulation was apparent at 50° or 70° C. under the conditions investigated.

The Formation of DDT from 1-(4-Chlorophenyl)-2,2,2-trichloroethanol

The reaction between the alcohol intermediate and chlorobenzene in sulphuric acid was studied in a manner similar to that described previously for the chloral–chlorobenzene reaction, by stirring the reactants in 50 ml. flasks placed in a thermostat. The reaction was quenched and the product was analyzed as usual.

It was found that the yield and rate of DDT production depended on the temperature, sulphuric acid concentration, and amount in much the same way as the chloral–chlorobenzene reaction. Depending on the reaction temperature used, two types of rate curves have been found; representative ones are plotted in Fig. 8.

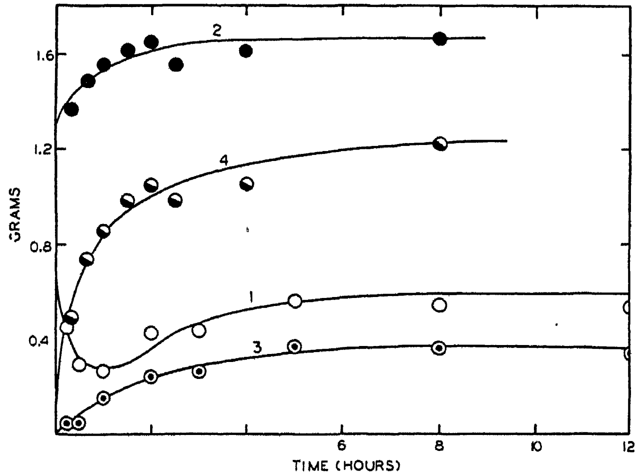


FIG. 8. *Rate of conversion of intermediate alcohol to crude product at 0° C.—1, at 30° C.—2, and to p,p′-DDT at 0° C.—3, and at 30° C.—4.*

It is apparent that the purity of the crude product increases as the reaction proceeds, but as has been previously pointed out, the *p,p′*-DDT:total DDT ratio is constant throughout a reaction at a given temperature, so that the observed increase in purity is due to the disappearance of the alcohol concurrently with the formation of DDT.

A closer examination of Fig. 8 shows that at 0° C. the rate of disappearance of the alcohol is greater than the rate of appearance of DDT since the crude weight during the early parts of the reaction is less than the weight of alcohol used initially. To estimate the extent of loss due to the analytical method, the errors in the various steps have been assessed experimentally. Washing the chloroform solution of the crude material and distillation of the wet chloroform are sources of considerable error and together may amount to 22%. Hence, 140 mgm. of the 650 mgm. of alcohol put into a normal reaction mixture might be lost. Since 380 mgm. of crude material has been removed from the reaction mixture in one hour, as shown by the rate curves at 0° C., experimental error is not the sole factor responsible for the low crude yields encountered. It also indicates that, while the crude rate curves are not quantitatively correct, they do indicate the general behavior of the reaction.

A possible explanation of the low yields encountered at 0° C. is the rapid formation of an intermediate compound from the alcohol and conversion of it at a slower rate to DDT. This material should be water soluble or volatile at 50° C. at 1 mm. of mercury pressure to account for the lower crude yields.

The concentration of this hypothetical intermediate can be calculated as follows: The concentration of the original alcohol in the crude product can be calculated in a manner similar to that used previously in the normal Baeyer condensation; from the constancy of the *p,p′*-DDT:total DDT ratio and the final purity of 85% achieved in these reactions at 0° C., starting with pure 1-(4-chlorophenyl)-2,2,2-trichloroethanol, the total DDT content of the product can be calculated from the *p,p′*-DDT yield. Since the crude product weight represents the alcohol plus DDT, the difference between the weight of crude and the weight of DDT at a given time gives the weight of the alcohol at that time. The intermediate concentrations can then be derived by adding the percentages of the alcohol present as such and in DDT and subtracting the sum from 100%. The difference represents the per cent intermediate, and these values, together with the alcohol values, are plotted in Fig. 9. During the process of calculation from the original data the errors are magnified by multiplication and especially by subtraction of quantities of comparable magnitude. Consequently, the data used for calculation were taken from the smoothed curves in Fig. 8.

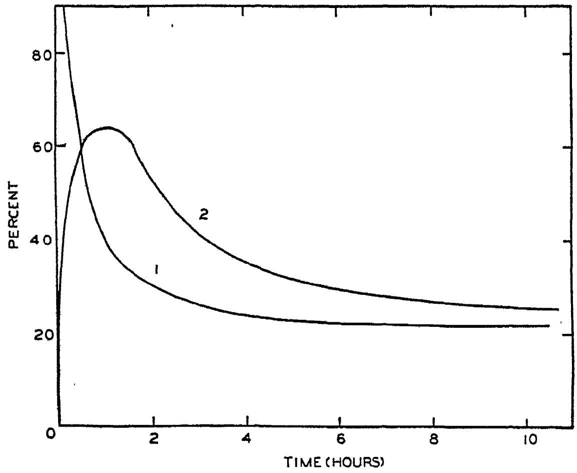
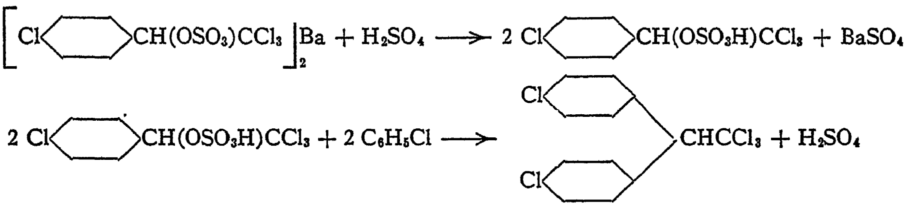


FIG. 9. *Rate of decrease of the alcohol concentration at 0° C.—1, and intermediate concentration—2.*

Since the intermediate may be 1-(4-chlorophenyl)-2,2,2-trichloroethyl bisulphate as proposed by Rueggeberg, and since it might be expected to be water soluble, thus explaining the low crude yields encountered at 0° C., an attempt was made to isolate this material from a normal reaction mixture in the form of its barium salt, but this was not successful.

However, a barium salt has been isolated from the reaction of dioxane sulphotrioxide and the alcohol. Assuming the residue from the ignition of this product to be barium sulphate, the yield of the barium salt of 1-(4-chlorophenyl)-2,2,2-trichloroethyl bisulphate was 43%.

If the free bisulphate ester, 1-(4-chlorophenyl)-2,2,2-trichloroethyl bisulphate, is an intermediate between the alcohol and DDT, its barium salt should form DDT with sulphuric acid and chlorobenzene according to the following series of reactions



It was found that when 3 gm. of the barium salt was allowed to react with 2 ml. (0.0198 mole) of chlorobenzene and 10 ml. (0.188 mole) of sulphuric acid (101.0% H_2SO_4) a yield of 1.464 gm. of crude DDT was obtained. This represents a 57% yield based on the anhydrous salt of the sulphuric acid ester.

Discussion

Mechanism of the Reaction

The fact that sulphuric acid forms complexes with chloral, and esters with the alcohol, does not necessarily indicate that they are intermediate in a normal Baeyer condensation. There is considerable evidence that aldehydes form oxonium ions in the presence of concentrated sulphuric acid, and also that alcohols form carbonium ions in the same solvent. By analogy it might be expected that similar ions form with chloral and 1-(4-chlorophenyl)-2,2,2-trichloroethanol in the Baeyer condensation so that the reaction mechanism may be presented:

$$CCl_3CHO + H_2SO_4 \rightleftharpoons CCl_3CHOH^+ + HSO_4^- \qquad \text{I}$$

$$CCl_3CHOH^+ + C_6H_5Cl + HSO_4^- \longrightarrow ClC_6H_4CH(OH)CCl_3 + H_2SO_4 \qquad \text{II}$$

$$ClC_6H_4CH(OH)CCl_3 + 2\,H_2SO_4 \rightleftharpoons ClC_6H_4CHCCl_3^+ + H_3O^+ + 2\,HSO_4^- \qquad \text{III}$$

$$ClC_6H_4CHCCl_3^+ + C_6H_5Cl + HSO_4^- \longrightarrow (ClC_6H_4)_2CHCCl_3 + H_2SO_4 \qquad \text{IV}$$

Since the alcohol accumulates in the crude during the early portions of the reaction at 0° C. with acid concentrations below 98.5% or at 30° C. with low acid amounts and concentrations, the rates of formation of the alcohol and DDT must be about the same; under other conditions the rate of formation of the alcohol must determine the rate of the over-all reaction. Whether

Reaction I or Reaction II involved in the formation of the alcohol is rate determining is not clear, although it may be Reaction I since it involves sulphuric acid which has been shown to have an important influence on the reaction.

This mechanism also explains the low crude yields encountered in the early parts of the reaction of 1-(4-chlorophenyl)-2,2,2-trichloroethanol to form DDT at 0° C. The formation of carbonium ion may proceed to equilibrium at a rate faster than its subsequent reaction to form DDT, so that early in the reaction it is present in the sulphuric acid as carbonium ion. If the sulphuric acid is quenched at this time the carbonium ion will be largely converted to the sulphuric acid ester by the reaction

$$ClC_6H_4CH(OH)CCl_3 + HSO_4^- \longrightarrow ClC_6H_4CH(OSO_3H)CCl_3$$

the rate of which is increased by the large concentration of bisulphate ion from dilution of the sulphuric acid. Since the sulphate may be expected to be soluble in this medium it is thus removed from the crude product. This behavior is not encountered at 30° C. because Reaction IV must proceed at a rate sufficient to keep the carbonium ion concentration small.

At acid concentrations near 100% the effect of a still more effective catalyst, sulphur trioxide may be imposed on the sulphuric acid.

Since an increase in the amount or concentration of sulphuric acid or an increase in reaction temperature generally results in lower *p,p'*-DDT yields, although the time for complete reaction will be shorter, the choice of optimum reaction conditions will depend on the equipment employed. In order to meet purity specifications it may be necessary to recrystallize the crude product, unless the purity is increased sufficiently by using lower temperatures or 4-chlorobenzenesulphonic acid (spent acid containing 4-chlorobenzenesulphonic acid could be fortified with sulphur trioxide and reused).

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STUDIES ON THE FORMATION OF HEXAMINE FROM FORMALDEHYDE AND AMMONIUM SALTS IN AQUEOUS SOLUTION[1]

By J. R. Polley[2], C. A. Winkler[3], and R. V. V. Nicholls[4]

Abstract

It is shown that the reaction of formaldehyde with an ammonium salt to form hexamine is general. The rate of formation and the final yield of hexamine vary greatly with the different ammonium salts, being greater in the solutions of higher pH. When buffered at given pH, the various ammonium salts give approximately the same rates of formation and final yields of hexamine. Rate curves have been determined for the reaction of formaldehyde with ammonium nitrate in aqueous solutions buffered at pH 8.0, 6.0, and 4.0, at temperatures of 0°, 20°, and 40° C. and over a range of initial mole ratios (formaldehyde: ammonium nitrate) of 0.75 to 3.0. For each set of conditions, three rate curves have been obtained on the basis of ammonia consumed, formaldehyde consumed, and material precipitated with mercuric chloride. In excess formaldehyde, it appears that a stable by-product is formed; its formation increases as the temperature is increased. In excess ammonium nitrate, by-product formation is decreased. A mechanism of hexamine formation is suggested in accordance with the data.

Introduction

The kinetics of the reaction between formaldehyde and ammonia in aqueous solution to produce hexamine were first studied by Baur and Rüetschi (1) in 1941 and more recently in greater detail by Boyd and Winkler (2).

Although hexamine has been prepared by the reaction of formaldehyde with certain ammonium salts, in both aqueous and glacial acetic acid solutions (3, 10, 12, 13), there has been no investigation of the kinetics of hexamine formation in such reactions. At least two different reaction sources should be possible. When the formaldehyde functions as a condensing agent, hexamine is formed. Formaldehyde may act, however, as a reducing agent, in which case the salts of methylamines are formed (6, 7).

$$NH_4Cl \xrightarrow{HCHO} CH_3NH_2 . HCl \longrightarrow (CH_3)_2NH . HCl \longrightarrow (CH_3)_3N . HCl + nHCOOH$$

If the reaction of formaldehyde to form hexamine is general with ammonium salts, the equation can be written in the general form:

$$6HCHO + 4NH_3 . HX \longrightarrow (CH_2)_6N_4 + 6H_2O$$

It was proposed in this present work to determine whether the reaction was general for different ammonium salts by investigating the reaction of formaldehyde with numerous ammonium salts in both aqueous and glacial acetic acid media. In particular, it was hoped to isolate and identify hexamine either as such or as one of its salts, but, failing this, to establish its presence in the

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Contribution from the Physical and the Organic Chemistry Laboratories, McGill University, Montreal, Que.

[2] *Graduate student and demonstrator.*

[3] *Professor of Chemistry.*

[4] *Associate Professor of Chemistry.*

reaction solution by the addition of mercuric chloride to the acidified solution, with a view to precipitating the insoluble hexamine – mercuric chloride complex (8).

Experimental and Results

The isolation of hexamine from various aqueous formaldehyde–ammonium salt solutions was attempted by evaporating them to dryness under reduced pressure at 50° C. The mercuric chloride method indicated the presence of some hexamine in all the reaction solutions, but hexamine was isolated and identified only when ammonium carbonate, acetate, and propionate were used. It was found, however, that hexamine could be isolated in good yield with all the ammonium salts tried, if, before beginning the evaporation under reduced pressure, the reaction solution is made alkaline, for example, by the addition of sodium carbonate, sodium bicarbonate, etc.

Similarly, when the above procedure was used but with a glacial acetic acid solution of paraformaldehyde and the ammonium salt, hexamine was shown to be present in all the reaction solutions but was isolated in good yield only with ammonium acetate, propionate, and carbonate. Hexamine was obtained in good yield with all the ammonium salts tried if the last quarter of the distillation were conducted in the presence of barium carbonate.

Thus, it appears that the reaction of formaldehyde with an ammonium salt to form hexamine is general, the isolation of the hexamine in good yield depending on the neutralization of the acid liberated in the reaction before the reaction solution is evaporated to dryness.

A study was next made of the rate of hexamine formation in aqueous solutions of formaldehyde with different ammonium salts. The reactions were conducted in glass-stoppered Erlenmeyer flasks. The formation of the hexamine – mercuric chloride complex was used for the quantitative estimation of hexamine as it was by Hale (5),[1] Garmaise (4), and Boyd and Winkler (2). The rate of hexamine formation was studied in solutions initially 2.5 N in ammonium salt and 3.75 N in formaldehyde by precipitating the hexamine in 4-ml. samples of the reaction solution after given time intervals by the addition of mercuric chloride solution. The weight of hexamine was determined from a calibration curve between given weights of hexamine and the corresponding weight of the hexamine – mercuric chloride complex.

The rate of hexamine formation from formaldehyde with a series of ammonium salts was investigated by this procedure. The effect of varying the formaldehyde: ammonium salt ratio on the rate of hexamine formation was also investigated. The formaldehyde concentration was doubled in one series of experiments while in another series the ammonium salt concentration was doubled. Fig. 1 shows the rate of hexamine formation with different ammonium salts and Fig. 2 shows the effect of varying the formaldehyde: ammonium salt ratio on the rate of hexamine formation with a given ammonium salt.

It is seen that doubling the formaldehyde concentration beyond that required by the theoretical ratio produces a larger increase in the rate of formation and final yield of hexamine than is observed when the ammonium

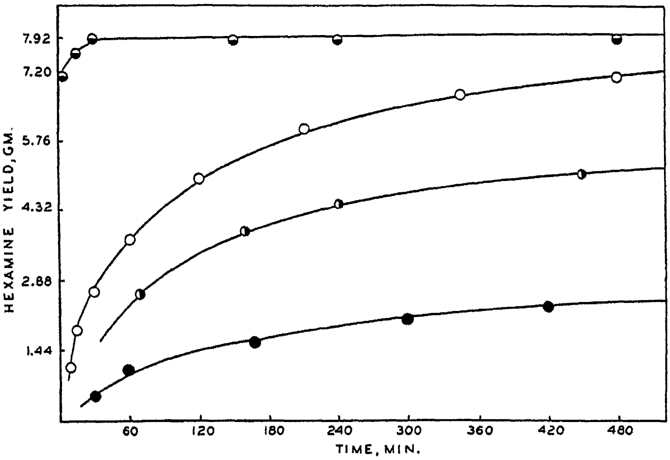


FIG. 1. *Rate of hexamine formation with different ammonium salts.*
◒—CH_3COONH_4. ○—$(COONH_4)_2$. ◑—$(NH_4)_2SO_4$. ●—NH_4NO_3.

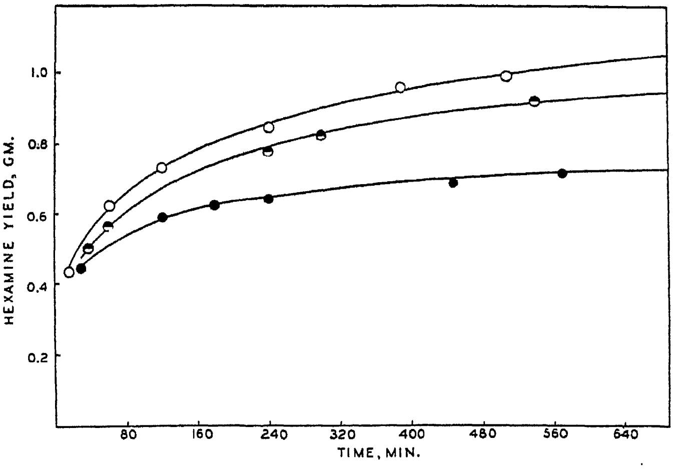


FIG. 2. *Rate of hexamine formation at 25° C. in dilute formaldehyde – ammonium sulphate solutions.* ○—*Mole ratio HCHO : NH_3 of 3 : 1.* ◒—*Mole ratio HCHO : NH_3 of 1.5 : 2.* ●—*Mole ratio HCHO : NH_3 of 1.5 : 1.*

salt concentration is doubled. It was also noted that the pH of the formaldehyde – ammonium nitrate solution was lower than that of formaldehyde – ammonium acetate solution, both at the beginning of the reaction and at the end point. This observation suggested that the pH of the medium might be one of the most important factors governing the rate of formation.

The effect of pH on both the rate of hexamine formation and the final yield was studied in aqueous formaldehyde – ammonium salt solutions by repeating the previous experiments except that this time the solutions were buffered at pH 4.0, 6.0, and 8.0. Fig. 3 shows the rate of hexamine formation with

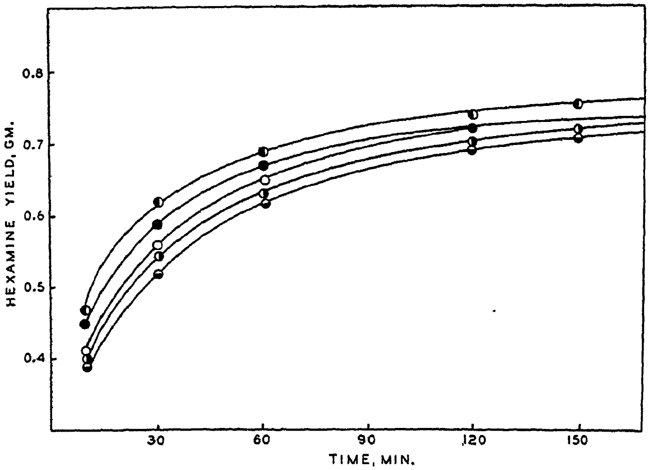


FIG. 3. *Rate of hexamine formation at 25° C. in various formaldehyde – ammonium salt solutions buffered at pH 4.0.*
◐—*$(NH_4)_2HPO_4$*. ●—*CH_3COONH_4*. ○—*$(COONH_4)_2$*. ◑—*$(NH_4)_2SO_4$*. ◒—*NH_4NO_3*.

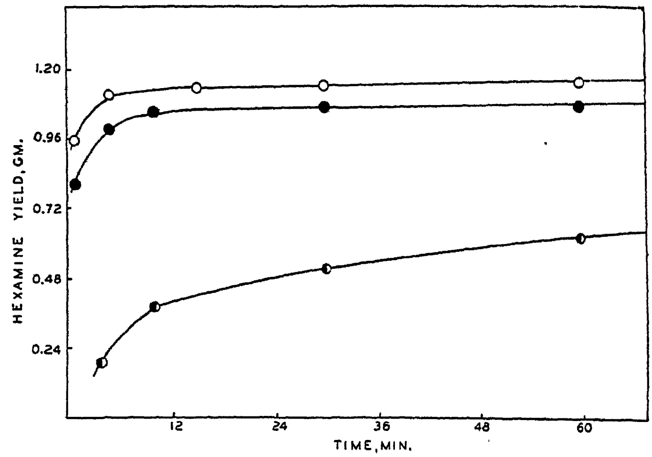


FIG. 4. *Rate of hexamine formation at 25° C. in buffered formaldehyde – ammonium nitrate solutions.*
○—*At pH 8.0.* ●—*At pH 6.0.* ◐—*At pH 4.0.*

different ammonium salts when the solutions were buffered at pH 4.0. Similar results were obtained at pH 6.0 and 8.0. Fig. 4 shows the effect of pH on the rate of hexamine formation with a given ammonium salt.

These graphs present a striking illustration of the effect of pH on both the rate of hexamine formation and the final yield. In buffered solution, the rates are closely similar for the different ammonium salts used, and the final yields differ by only about 10%, whereas in unbuffered solutions, the yields differ by as much as 60%.

These observations suggest that, at given pH, all the ammonium salts give approximately the same rates of formation and final yields of hexamine, indicating that, at given pH, different ammonium salts lose their individuality and become merely sources of ammonium ions or available ammonia as far as hexamine formation is concerned.

A kinetic study of the formation of hexamine in an aqueous formaldehyde – ammonium salt solution was then made, the rate of disappearance of ammonia and formaldehyde being followed as well as the rate of appearance of hexamine. Since it was shown that at given pH the various ammonium salts show similar rates of hexamine formation, these experiments were made using ammonium nitrate as a representative salt.

Formaldehyde – ammonium nitrate solutions buffered at pH 4.0, 6.0, and 8.0 were used. To facilitate buffering these reactions, the ammonium nitrate concentration was reduced to 0.20 *N* and the formaldehyde concentration to 0.30 *N*. The buffer solutions were prepared according to McIlvaine but five times the recommended concentrations were used to ensure an adequate alkali reserve in the buffered solutions. Temperatures of 0°, 20°, and 40° C. were also used. The effect on the rate of formation and the final yield of hexamine of doubling the concentration of the formaldehyde and the ammonium nitrate beyond the theoretical ratio was also studied in the solutions at the pH levels and temperatures indicated above.

The course of hexamine formation in the reaction solutions was followed by removing 4-ml. samples after different times and adding to 20 ml. of acidified saturated mercuric chloride solution. A hexamine – mercuric chloride complex calibration curve was established for each pH of the reaction mixture investigated. This was necessary, since the addition of 4-ml. samples of these different buffered solutions to the mercuric chloride solution resulted in slightly different pH of the medium from which the hexamine was precipitated and this caused a shift in the calibration curve.

The formaldehyde content of the solution was determined by the method of Schulek (11) which is a variant of the well known potassium cyanide method of Romijn (9). The procedure is based on the quantitative formation of cyanohydrin when formaldehyde is treated with a solution containing a known excess of potassium cyanide. The method involves determining the unreacted cyanide by iodimetry.

The residual ammonia, as ammonium nitrate, at any given time in the reaction solution could not be determined directly by the Kjeldahl method since hexamine was also present. Therefore, the method used involved the determination of the ammonia present in the 4-ml. sample for the hexamine analysis. After the hexamine – mercuric chloride complex was collected on a tared, sintered-glass crucible, the filtrate was collected for a determination of the residual ammonia. The excess mercury was precipitated with sodium sulphide solution to prevent the formation of mercury–ammonia complexes. After removing the mercurous sulphide precipitate by filtration, the solution was placed in a 125 ml. Kjeldahl flask and the ammonia determined by the usual Kjeldahl method.

For each set of reaction conditions, three rate curves of hexamine formation were obtained on the basis of ammonia consumed, formaldehyde consumed, and material precipitated with mercuric chloride. In all, this gave rise to 27 graphs but since only three different types of behavior were observed, it is necessary to reproduce only three typical graphs for discussion.

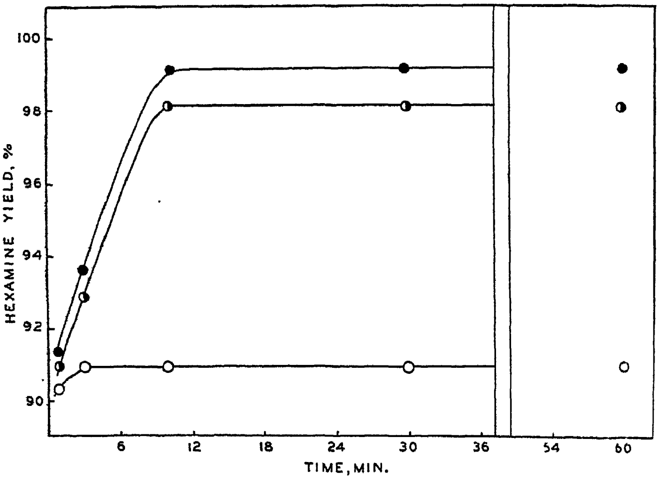


FIG. 5. *Rate curves for reaction at pH 8.0 and 40° C. Mole ratio formaldehyde : ammonium nitrate of 3 : 1.*

●—*Yield based on NH_3 consumed.* ◑—*Yield based on HCHO consumed.* ○—*Yield based on precipitate with $HgCl_2$.*

Fig. 5 represents the type of behavior that is observed in excess formaldehyde. The mercuric chloride curve is about 10% below the formaldehyde curve at the end point, although the curves are in closer agreement initially. The ammonia curve is about 3% above the formaldehyde curve. The fact that both the formaldehyde and ammonia curves lie above the mercuric chloride curve suggests that more formaldehyde and ammonia are consumed than appear as hexamine. In view of the manner in which the data are expressed, it would seem necessary to assume the formation of a by-product, the formation of which increases as the temperature is raised but appears to be essentially independent of the pH. No attempt was made to identify the by-product, the purpose of this study being the conversion of reactants to hexamine. It would be difficult to isolate and identify a by-product, if formed, in the presence of formaldehyde, ammonium nitrate, buffering reagents, and hexamine, and at such dilution and in such small amount (the conversion of reactants to hexamine being at least 90%). In excess formaldehyde, the three rate curves differ only slightly at first. With increasing time, however, the mercuric chloride curve indicates that an end point has been reached, while the formaldehyde and ammonia curves continue to rise. This shows that hexamine formation has ceased but formaldehyde and ammonia are still reacting. These observations suggest that, under the reaction conditions investigated, the formation of hexamine is a more rapid reaction than that of by-product formation.

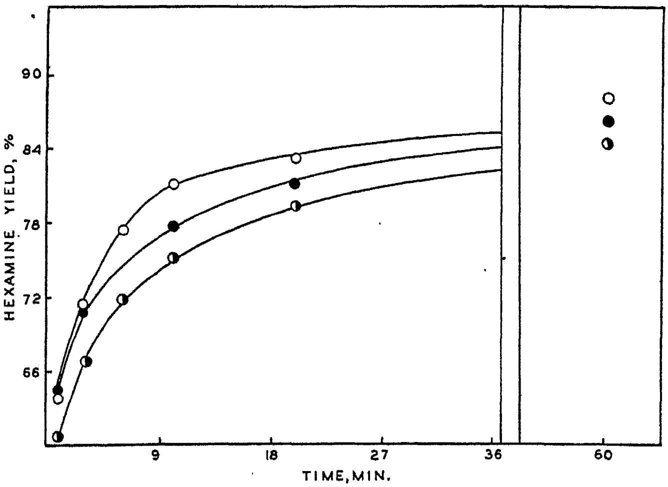


FIG. 6. *Rate curves for reaction at pH 8.0 and 20° C. Mole ratio formaldehyde: ammonium nitrate of 1.5 : 1.*

●—*Yield based on* NH_3 *consumed.* ◑—*Yield based on HCHO consumed.*
○—*Yield based on precipitate with* $HgCl_2$.

Fig. 6 represents the type of behavior frequently observed when the formaldehyde and ammonium nitrate are present in the theoretical ratio and observed in excess ammonium nitrate at pH 8.0. The ammonia curve lies below the mercuric chloride curve but both of these curves lie above the formaldehyde curve. Since it is not possible to have more hexamine formed than can be accounted for on the basis of formaldehyde consumed, it is evident that an explanation must be provided for these analytical results.

One possible explanation is that the hexamine – mercuric chloride complex adsorbs ammonium nitrate or ammonia, thereby adding extra weight to the complex. Actually, however, excess ammonium nitrate does not produce a greater divergence in the curves. An experiment in which hexamine was precipitated in the presence of ammonium nitrate according to the procedure outlined for hexamine analysis showed that there was no co-precipitation or adsorption.

The other possible explanation is that some material other than ammonium nitrate or hexamine is co-precipitated with the hexamine. This would account for the high mercuric chloride curve. The fact that the ammonia curve is also higher than the formaldehyde curve may be explained if the material co-precipitated with the hexamine also contains ammonia, thereby resulting in an abnormally high consumption of ammonia. The observation that the formaldehyde curve lies below the ammonia and mercuric chloride curves may be explained by assuming that, in the analysis of the reaction solution for residual formaldehyde, formaldehyde is analysed out of the material, which may be an intermediate.

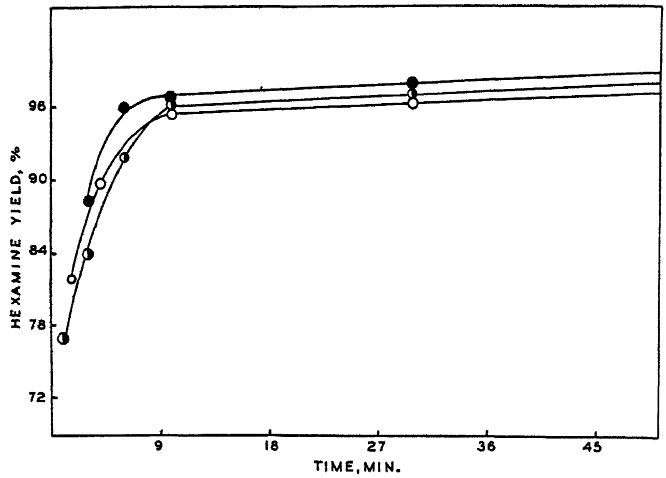


Fig. 7. *Rate curves for reaction at pH 8.0 and 20° C. Mole ratio formaldehyde : ammonium nitrate of 1.5 : 2.*

●—*Yield based on NH_3 consumed.* ◑—*Yield based on HCHO consumed.*
○—*Yield based on precipitate with $HgCl_2$.*

Fig. 7 represents the behavior observed in excess ammonium nitrate. The three rate curves are closer together than they are in excess formaldehyde and when the reactants are present in the theoretical proportions for hexamine formation. Thus, whereas excess formaldehyde decreases the conversion of reactants to hexamine, excess ammonium nitrate favors the conversion of reactants to hexamine.

A further important observation disclosed by the data is that doubling the formaldehyde concentration beyond that required by the theoretical proportions for hexamine formation produces a greater increase in the initial rate of hexamine formation than is produced by doubling the ammonium nitrate concentration. Also, the final hexamine yields are usually greater in excess formaldehyde at the lower temperatures. As the temperature is increased, however, the conversion of the reactants to hexamine becomes less complete, so that the yield of hexamine at the end point may be actually decreased.

In their investigation of the aqueous formaldehyde–ammonia system, Baur and Rüetschi (1) followed the course of the reaction only by an acid titration of the ammonia. They favored a mechanism of hexamine formation that involved the formation of methyleneimine and its subsequent trimerization to the postulated intermediate, cyclotrimethylenetriamine. Since they followed only the rate of disappearance of ammonia and did not simultaneously follow the rate of disappearance of ammonia and the rate of appearance of hexamine, it is impossible to compare their results with those obtained in this kinetic study of the aqueous reaction of formaldehyde with ammonium nitrate at various controlled pH.

Boyd and Winkler (2), on the basis of their more detailed kinetic study of the aqueous formaldehyde–ammonia system, proposed a two-path mechanism of hexamine formation, one path being preferred in excess ammonia, the other in excess formaldehyde. Formaldehyde and ammonia are represented as reacting in a series of addition and condensation reactions, excess ammonia leading to the formation of cyclotrimethylenetriamine as intermediate, whereas excess formaldehyde leads to the formation of the methylol form of hemi-hexamine, which on dimerization yields hexamine.

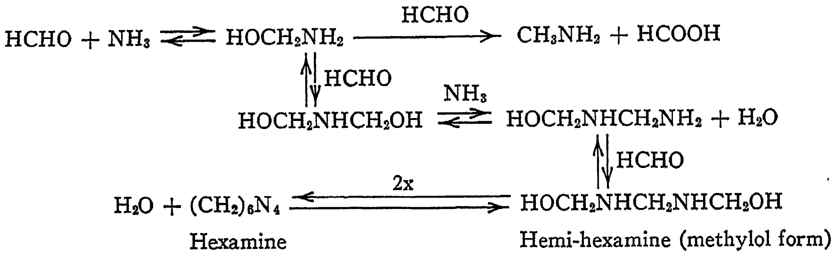
In this present study of the aqueous reaction of formaldehyde with ammonium nitrate at various controlled pH, it has also been found that the three rate curves tend to be in close agreement in excess ammonium nitrate but to diverge in excess formaldehyde. However, whereas Boyd and Winkler found that this effect was reversed at elevated temperature, the data in the present investigation indicate that elevated temperature merely accentuates the tendency for by-product formation, especially in excess formaldehyde. Since, in the work of Boyd and Winkler, the pH of the different reaction solutions was not known nor controlled, it is difficult to say whether the difference between the results is fundamental. In any event, the present study at controlled pH gives no indication of alternative reaction paths leading to hexamine formation.

If it be assumed that the active reagent in the ammonium salt with which the formaldehyde reacts to form hexamine is ammonia, then the equilibrium involving ammonia and hydrogen ion will explain the effect of pH on the rate.

$$NH_3 + H^+ \rightleftarrows NH_4^+$$

If the active reagent were the ammonium ion, the reaction should proceed readily under conditions favoring the formation of ammonium ions, that is, in acidic solutions. The experimental data, however, show that the reaction is favored in solutions of higher, not lower pH.

On the basis of the data obtained from these experiments, the following mechanism of hexamine formation from the aqueous reaction of formaldehyde with an ammonium salt is suggested.



$$\begin{tikzcd}
HCHO + NH_3 \arrow[r, leftrightarrow] & HOCH_2NH_2 \arrow[r, "HCHO"] \arrow[d, leftrightarrow, "HCHO"] & CH_3NH_2 + HCOOH \\
& HOCH_2NHCH_2OH \arrow[r, leftrightarrow, "NH_3"] & HOCH_2NHCH_2NH_2 + H_2O \arrow[d, leftrightarrow, "HCHO"] \\
H_2O + (CH_2)_6N_4 \arrow[rr, leftrightarrow, "2x"] & & HOCH_2NHCH_2NHCH_2OH
\end{tikzcd}$$

Hexamine

Hemi-hexamine (methylol form)

The first intermediate represented is methylolamine, $HOCH_2NH_2$. If formaldehyde reacts with methylolamine in an addition reaction, dimethylolamine, $HOCH_2NHCH_2OH$, is formed. If, however, formaldehyde reacted with it in an oxidation–reduction reaction, methylamine would be formed. The formation of methylamine is represented as an irreversible reaction, since it was shown that hexamine was not formed from it. If it be considered that the methylolamine reacts with ammonia instead of with formaldehyde, methylenediamine, $H_2NCH_2NH_2$, would be formed. This, on reaction with formaldehyde, would also yield the methylol form of hemi-hexamine.

The experimental observation that the rate of hexamine formation is more sensitive to change of formaldehyde concentration than to change of ammonia concentration is then readily explained if it be assumed that the rate of reaction between formaldehyde and amino groups is rate-governing.

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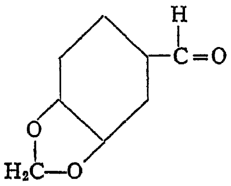
THE ISOLATION OF SASSAFRAS LIGNIN[1]

By W. J. Bond,[2] Irvine G. Goddard,[3] and George F Wright[4]

Abstract

Since the sassafras tree yields oils which are rich in safrole, it might be expected that the lignin from the wood would contain the piperonyl nucleus. This lignin was extracted from the wood with hot acetic acid and was found to resemble lignins from other deciduous woods in methoxyl content and solubility. It did contain much combined carbohydrate which seemed to be pectic in nature, since it was removed by boiling formic acid with evolution of carbon dioxide and formation of furfural. No piperonylic acid could be isolated from these lignin fractions by alkaline permanganate or hydrogen peroxide oxidations. Sassafras ligninsulphonic acid was prepared and then distilled with alkali but no piperonal was found in the distillate. According to these criteria, sassafras lignin contains none of the methylenedioxy linkage characteristic of the piperonyl nucleus.

In 1927 Freudenberg (4) suggested that lignin contained a methylenedioxy linkage, since he obtained 0.2 to 1.2% yields of formaldehyde by distilling suspensions of beech or spruce lignins with 12% hydrochloric acid. He considered that this methylenedioxy group was linked as in piperonal, I, an analogue of the vanillin and syringaldehyde which have been isolated from spruce and birch lignins (5).



I

Sarkar (8) also concluded that this linkage was present in the lignin molecule. By distillation of jute lignin with 28% sulphuric acid he was able to obtain formaldehyde yields as high as 2.6%.

Phillips and Goss (7), on the other hand, found that, while Freudenberg's results could be checked in the case of spruce lignin, other lignins, prepared in different ways, gave varying amounts of formaldehyde, and some lignins gave no formaldehyde. It appeared to them that both the source of the lignin and its method of isolation were factors governing the formaldehyde yield.

When Hunter, Wright, and Hibbert (6) subjected substances like piperonal, dihydrosafrole, and piperonylic acid to some of the extraction conditions used for isolation of lignin, they found that 75 to 88% of the aromatic compounds could be recovered unchanged. This indicated that unaltered methylenedioxy linkages might be expected in lignins. They found, however, that the 12% hydrochloric acid used by Freudenberg was not very effective toward splitting of formaldehyde from piperonylic acid although 28% sulphuric acid effected a scission which was almost quantitative.

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Contribution from the Chemical Laboratory, University of Toronto, Toronto, Ont.

[2] *Undergraduate Student.*

[3] *Graduate Student.*

[4] *Professor of Chemistry.*

They ascertained further that many carbohydrates yielded formaldehyde, as well as furfural, when boiled with acid. Since these two aldehydes were also isolated concomitantly from a number of lignins, they concluded that they were formed from carbohydrate incompletely removed from (or intrinsic with) the lignins. Freudenberg (3) questioned this conclusion, although he points out that cinnamyl alcohol types rather than methylenedioxy types may be the source of his formaldehyde.

It occurred to the present authors that, of all lignins which might be expected to contain the methylenedioxy linkage, that isolated from sassafras wood ought to be the richest in this characteristic, since the oils from this wood are rich in safrole (10). The methods which yield vanillin and vanillic acid from woods like spruce, birch, and oak (whose oils are rich in guaiacyl compounds) ought then yield piperonal and piperonylic acid from sassafras lignin.

Sassafras xylem reduced to 25 mesh was extracted exhaustively with benzene–ethanol and from separate portions were then extracted acetic acid lignins (1), and ligninsulphonic acid.

These extractions were normal in every respect except that more trouble was encountered in freeing the isolated lignin from carbohydrate than was experienced with spruce or birch wood. Acetic acid extracted 24% of the weight of the wood as lignin, but this lignin contained combined carbohydrate. Much of this carbohydrate, which seemed to be of a pectic acid nature, could be liberated by further digestion with 95% formic acid.

The acetic acid lignin was fractionated. Successive Soxhlet extractions of this acetic acid lignin with ether, benzene, and chloroform removed 14, 16, and 70%, respectively, of the total lignin, the corresponding methoxy contents being 21.9, 20.8, and 19.5%. These values resemble those obtained for comparable values of birch lignin. Since a cyclic acetal such as is found in piperonal gives no methyl iodide in the Zeisel determination it is evident from these methoxyl values that the methylenedioxy linkage is not present instead of methyl ether linkages to any appreciable extent.

The lignin sulphonic acid was prepared from the sassafras xylem by a standard cooking procedure. The liquor was then boiled with alkali and the aqueous distillate continuously extracted with benzene and then returned to the boiling alkaline solution. This variation from the prescribed procedure (9) would be expected to separate piperonal, which is volatile in boiling aqueous alkalis, from vanillin and syringaldehyde which are not volatile. However, no residue remained after evaporation of the benzene. Since piperonal was shown to be stable to alkaline heating and to respond to the extraction procedure, it is probable that no piperonyl linkage is present in sassafras ligninsulphonic acid.

A further attempt to discover the presence of the piperonyl nucleus was made by oxidation of the sassafras lignin. Although alkaline potassium permanganate would convert piperic acid (2) to piperonylic acid in 66% yield, a comparable oxidation of the ether-soluble fraction of the lignin yielded none of this easily sublimed acid.

In connection with these oxidation studies, it was found that alkaline hydrogen peroxide would oxidize piperonal in 88% yield to piperonylic acid, although it would not attack piperic acid. The strong hydrogen peroxide (15%) did, however, attack the lignin smoothly and efficiently in alkaline solution. When piperonal to the extent of 1.2% was added to the lignin, it was recovered from the oxidizing medium as a 48% yield of piperonylic acid. On the other hand no trace of this acid was obtained from the lignin alone.

In view of these results it would seem doubtful that sassafras lignin contains a measurable amount of the piperonyl nucleus.

Experimental

Preparation and Purification of the Woodmeal

A sassafras tree, approximately 15 years old (27 rings) growing at Simcoe, Ontario, was found in a clearing on sandy loam soil. A 28 in. section of the tree trunk, 5 to 5½ in. in diameter, about 40 in. from the soil surface, was taken.

The bark and cambium were carefully removed and the xylem, first made into shavings by means of a lathe and chisel, was put through a Wiley mill to prepare the woodmeal (25 mesh). The woodmeal was air-dried; it contained about 9.4% moisture.

Extraction of Sassafras Woodmeal with Acetic Acid

A suspension of 400 gm. of this purified sassafras woodmeal in 2.5 litres of glacial acetic acid was stirred under reflux for 100 hr. During this period, 4.2 cc. (N.T.P.) of carbon dioxide was evolved per gram of woodmeal. Finally 233 gm. of residual woodmeal was filtered off through linen cloth and washed with acetic acid. The filtrate and washings were concentrated to a volume of about 350 cc. (10 to 15 mm.) and then poured into 2 litres of water. The lignin precipitated in this manner was filtered off by gravity and washed with 35 litres of water until free from carbohydrate by Molisch test. There was some tendency toward peptization; the colloidal lignin in the first 5 litres of filtrate was precipitated by boiling, after addition of sodium sulphate, until the volume was 200 cc. The distillate gave a strong furfural test. The aqueous residue, from which the coagulated lignin was filtered, was extracted with 150 cc. of ether. The extract was distilled to yield 0.83 gm., b.p. 120° to 180° C. (0.001 mm.), which did not crystallize after six months. No piperonylic acid could be isolated after the oxidation of this distillate (in alkaline solution) with 200 ml. of 2% potassium permanganate solution. Oxidation of piperic acid under the same conditions, gave a 66% yield of piperonylic acid, m.p. 226° C.

The total of the precipitated lignin was dried at 50° to 60° C. (10 mm.) to weigh 81 to 84 gm. or 23 to 24% by weight of the oven-dry woodmeal. Although this material had been washed free from water-soluble carbohydrate, it undoubtedly contained combined carbohydrate, since a suspension in water gave a positive Molisch test. It was soluble in acetic and formic acids, ethyl acetate, acetone, dioxane, chloroform, pyridine, and dilute alkali. It was partly soluble in ether, benzene, methanol, and ethanol.

Fractionation of Acetic Acid Sassafras Lignin

Fractionation was carried out in a Soxhlet extractor, using ether at 760 mm., benzene at 200 mm., and chloroform at 250 mm. in this succession. The three solvent fractions, which comprised almost all the lignin, were evaporated, finally in a dry air stream, except for aliquot portions which were precipitated into petroleum ether (b.p. 28° to 38° C.) for methoxyl determination.

Removal of Combined Carbohydrate from the Chloroform Fraction

In order to remove the combined carbohydrate from the least soluble, chloroform fraction, 67 gm. of this lignin was boiled under reflux in 350 cc. of 95% formic acid for 18 hr. This treatment liberated 6.2 cc. of carbon dioxide per gram of lignin used. The solvent was distilled off completely under 15 mm. pressure. The residue was washed with two litres of water to remove soluble carbohydrate (positive Molisch test and two osazones, m.p. 172° to 174° C. and 155° to 156° C.) and then with ether to remove furfural and other ether-soluble material. The residual lignin weighed 38.5 gm. after drying at 50° to 60° C. (10 mm.). A solution of 1 gm. of this lignin in 9 : 1 acetone–water (15 cc.) was precipitated in a fine stream into 200 cc. of stirred anhydrous ether. Its methoxyl content was 17.4%.

Absence of Piperonal in Sassafras Ligninsulphonic Acid

A suspension of 5.0 gm. of solvent-extracted dry sassafras woodmeal was cooked in a glass bomb tube with 70 cc. of sodium bisulphite cooking liquor containing 6% total and 1.2% combined sulphur dioxide. The temperature was raised to 125° C. over a three hour period and maintained at 120° to 135° C. for 12 hr.

The cooled suspension was filtered to remove 2.8 gm. of extracted meal (56% of total). The filtrate was boiled for 12 hr. with 6% aqueous sodium hydroxide solution in a flask which was equipped with a modified Soxhlet extractor surmounted by a reflux condenser. The modification of the Soxhlet extractor involved an air-vented vertical outlet sealed to the top of the tube which normally would return solvent. Since this dispensed with the siphoning action, a layer of benzene could be maintained over a water seal in the body of the extractor. This benzene thus continuously extracted the aqueous distillate, which then returned to the boiling flask.

Treatment of the ligninsulphonic acid in this way yielded no trace of piperonal in the benzene layer, but when 0.5 gm. of piperonal was cooked with 250 cc. of 6% aqueous sodium hydroxide for 12 hr. in this extractor, the recovery was 0.24 gm. (48%) of material, m.p. 34° to 35° C. The identity of this recovered piperonal was authenticated by preparation of the 2,4-dinitrophenylhydrazone, m.p. 260° C.

Oxidation with Potassium Permanganate

A total of 27.9 gm. of potassium permanganate was required at the rate of 6 gm. per hour to oxidize a 2.5% alkaline solution of 20 gm. of chloroform-soluble formic acid lignin at 5° C. Although subsequent acidification of the filtrate showed that 95% of the lignin had been oxidized, no piperonylic acid could be isolated by sublimation of the continuous ether extract. Under identical conditions, piperonal was oxidized to piperonylic acid in 66% yield.

Oxidation with Alkaline Hydrogen Peroxide

A solution of 10 gm. of ether-soluble sassafras lignin in 750 cc. of 10% aqueous sodium hydroxide solution was added proportionately over four hours with 670 ml. of 26% hydrogen peroxide to a flask equipped for rapid stirring. The temperature was maintained at 30° to 40° C. and a trace of petroleum ether (b.p. 60° to 70° C.) was added to reduce foaming. After 12 hr. the temperature was increased to 78° C. until foaming (destruction of hydrogen peroxide) had ceased and a negative peroxide test was obtained. The slightly turbid solution which resulted after acidification was continuously extracted with ether. This ether extract, dried with anhydrous sodium sulphate, was subsequently sublimed at 100° to 240° C. (10 mm.). Although oxalic acid, succinic acid, and a low melting solid (m.p. 30° to 50° C.) could be isolated from the sublimate, no piperonylic acid was found. Under otherwise comparable conditions 10 gm. of ether-soluble lignin plus 0.12 gm. of piperonal yielded 0.061 gm. of piperonylic acid, m.p. 210° to 215° C. This 48% crude yield was washed with a little ether to free it from oily impurity, after which it melted at 228° to 229° C. A mixed melting point with authentic material was not lowered.

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A RAPID COLORIMETRIC METHOD FOR THE DETERMINATION OF LYSINE IN PROTEIN HYDROLYSATES[1]

By M. Boulet,[2] J. A. Nelson,[3] and W. D. McFarlane[4]

Abstract

A solution of chlorinated lysine develops a blue color when heated with phosphomolybdic–phosphotungstic acid. This color reaction, which will detect lysine at a concentration of 1 p.p.m., has been made the basis of a sensitive and rapid colorimetric method for the determination of lysine. Lysine and arginine are quantitatively separated from the other amino acids in a protein hydrolysate by adsorption on Decalso and the lysine content of the eluate is determined in the presence of arginine (which does not give the color reaction) by applying the color reaction after chlorination. Satisfactory recoveries of added lysine have been obtained from mixtures of amino acids and from a gelatin hydrolysate. The lysine content of several proteins has been determined and the results compared with those in the literature. In general the values obtained by the colorimetric method are intermediate between those obtained by isolation procedures and those by microbiological methods. The result of a determination on crystalline bovine serum albumin checked closely with the value obtained by the isotope dilution method.

Introduction

It was observed in this laboratory that if an aqueous solution of lysine is treated with a solution of sodium bromate–bromide in hydrochloric acid and the excess bromine removed with sodium arsenite, the resulting product gives an intense blue color when heated with Folins uric acid reagent (phospho-18-tungstic acid). This color reaction will detect lysine in a concentration of 1 p.p.m. Colors of varying intensity are also given by serine, threonine, phenylalanine, tyrosine, tryptophane, cystine, methionine, proline, hydroxyproline, leucine, histidine, and ornithine. No color is given by glycine, alanine, aspartic and glutamic acids, norleucine, valine, and arginine.

We also found that lysine and arginine are quantitatively separated from the other amino acids in a hydrochloric acid hydrolysate of proteins when, after the hydrolysate has been freed from excess hydrochloric acid by vacuum distillation, the residue is dissolved in 10% aqueous pyridine and the solution passed through a column of Decalso. Arginine and lysine are strongly adsorbed, histidine and ammonia are weakly adsorbed, and the other amino acids are not adsorbed. The traces of histidine and ammonia are washed out of the column with 10% aqueous pyridine and the arginine and lysine are then recovered by elution with dilute hydrochloric acid or 0.2 *M* sodium carbonate solution.

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Contribution from the Department of Chemistry, Faculty of Agriculture (McGill University) Macdonald College, Que. Macdonald College Journal Series No. 208.

[2] *Graduate Research Assistant. Holder of a Fellowship under the National Research Council, Ottawa, and later a Scholarship from the Scientific Research Bureau, Quebec Provincial Government.*

[3] *Graduate Research Assistant. Present address: Ciba Company, Limited, Montreal, Que.*

[4] *Professor of Chemistry. Now, Director of Research, Canadian Breweries Ltd., Toronto, Ont.*

After treating the hydrochloric acid eluate with a solution of sodium bromate–bromide in dilute hydrochloric acid and removing the excess bromine with sodium arsenite, the color reaction can be applied to determine lysine in the presence of arginine. Ornithine interferes but it is not present in acid hydrolysates of proteins, with the unique exception of tyrocidine (7). Hydroxylysine probably gives the reaction but it is rarely present in significant amounts.

A sensitive and rapid colorimetric method was developed (10) and satisfactory recoveries of added lysine were obtained from mixtures of amino acids and from a gelatin hydrolysate. The lysine content of several purified proteins was determined, and the values obtained were generally intermediate between those obtained by isolation procedures and those by microbiological methods. The result of an analysis of crystalline bovine serum albumin checked closely with the value obtained by the isotope dilution method.

The method was submitted to workers in other laboratories and to other workers in this laboratory. Several reports mentioned encountering difficulties due to the uncertainty of the bromination reaction. In repeated tests with the same solution of lysine, bromination for varying periods of time did not always give maximum reaction in the same reaction time, so that an error of 10% could easily occur unless several determinations were made on the same sample. It was, therefore, decided to investigate the method further with a view to stabilizing the bromination reaction.

The Reaction of Bromine with Lysine

The details of the procedure (10) were based on the knowledge that the bromination reaction was influenced by time, concentration of bromine, and the amount of lysine present. The reaction time for optimal color development was inversely proportional to the concentration of bromine. These facts suggested that an unstable intermediate product was formed in the reaction between bromine and lysine, and this intermediate combined with the phenol reagent to produce the blue compound, whereas its decomposition product did not give the color reaction. Because of this secondary reaction the time of bromination had to be closely controlled.

In an attempt to stabilize the reaction, the hydrogen ion concentration was varied by adding acid or alkali to the lysine solution. When 1 ml. *N* hydrochloric acid was added before bromination, the reaction was slowed down and the maximum, as measured colorimetrically with the phenol reagent, was only 60% of the value obtained under the standard conditions of bromination. The addition of alkali accelerated the reaction but the yield decreased rapidly with time. With increasing time of bromination the amount of reducing substance, as measured colorimetrically with the phenol reagent, reached a maximum and then decreased. This indicated that the substance that reduced the phenol reagent was formed as an intermediate and that at least two steps were involved in the complete reaction.

When the hydrochloric acid in the brominating reagent was replaced with sulphuric, phosphoric, or hydrobromic acid the reaction rate was markedly decreased, and the maximum reaction was obtained in two to three hours instead of two to three minutes. Furthermore, the maximum color intensity was much less when these acids replaced hydrochloric acid.

Evidently hydrochloric acid plays an important role in the bromination reaction and cannot even be replaced by hydrobromic acid. It may act as a catalyst or as a source of free chlorine, since it is known that free chlorine and free bromine are produced when bromic acid ($HBrO_3$) reacts with hydrochloric acid. Solutions of lysine treated with a solution of pure bromine in 0.2 *N* hydrochloric acid for periods up to 20 min. at room temperatures gave practically no color with the phenol reagent. The reaction with lysine may, therefore, be due to chlorine rather than bromine.

Chlorination of Lysine

The reagent was prepared by bubbling electrolytic chlorine gas from a cylinder through 0.2 *N* hydrochloric acid. Standard solutions of lysine were chlorinated for varying periods of time, the excess chlorine removed with sodium arsenite solution, and the color developed with the phenol reagent. The results are given in Fig. 1, in which the colorimeter readings are plotted against reaction time. It will be seen that the reaction reached completion in four minutes and apparently the chlorination product is stable for at least 20 min. The yield, and hence the sensitivity of the reaction, is comparable to that obtained with the original bromine reagent.

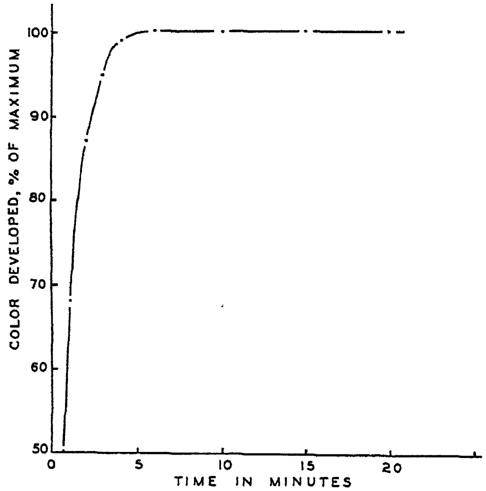

FIG. 1. *Chlorination of lysine for varying periods of time (lysine concentration = 2.88 μgm. per ml.).*

Variable results were obtained with chlorine prepared by oxidizing concentrated hydrochloric acid with manganese dioxide and purified by washing with a 5% solution of potassium permanganate. This was found to be due to the presence of chlorine dioxide, and the difficulty was eliminated by bubbling the chlorine through a 20% solution of barium chloride instead of the permanganate solution.

When chlorine was substituted for the bromine reagent in the determination of the lysine content of various proteins, the results obtained were substantially the same. However, the chlorination procedure is much simpler and more dependable.

Description of the Method

Reagents

(1). Decalso:— Sodium form of Decalso +40 to 60 mesh (Permutit Co. N.Y., water softener).

(2). Sodium chloride solution:—3 gm. sodium chloride (reagent grade) per 100 ml.

(3). Pyridine solution:—100 ml. of redistilled pyridine (b.p. 114° to 115° C.) diluted to 1 litre with distilled water. The solution is allowed to stand for a few hours before use, to permit the escape of air bubbles.

(4). Sodium carbonate solution (0.2 *M*):—2.12 gm. sodium carbonate (reagent grade) per 100 ml.

(5). Hydrochloric acid (2.0 *N*):—prepared by diluting constant boiling hydrochloric acid.

(6). Chlorine solution:—electrolytic chlorine gas from a cylinder, or chlorine gas generated by adding 3 gm. manganese dioxide to 12 ml. concentrated hydrochloric acid at a temperature not above 20° C., is bubbled through a 20% solution of barium chloride into 50 ml. 0.2 *N* hydrochloric acid for about 20 min. The chlorine solution should be used within one hour of its preparation.

(7). Sodium arsenite:—5 gm. sodium arsenite dissolved in 100 ml. water. The solution is freshly prepared each week.

(8). Mixed alkali:—A solution containing 2 gm. sodium citrate (reagent grade) and 4 gm. sodium phosphate dodecahydrate (reagent grade) per 100 ml.

(9). Phenol reagent:—prepared according to Folin and Ciocalteu (6) but with 100 gm. lithium sulphate monohydrate instead of 150 gm. per litre.

Preparation of the Adsorption Column

A weighed amount of Decalso (700 mgm.) is transferred to a beaker and washed by decantation three times with 3% sodium chloride, and then with distilled water until free from chloride. The adsorption apparatus consists of a 3 in., long stem Pyrex glass funnel, which has been constricted at the outlet. A small pad of cotton is inserted in the stem at the bottom, 25 ml. of water is poured into the funnel, and the adsorbent, suspended in water, is immediately added. By tapping the funnel gently an air-free column about 10 cm. long is obtained. A thin pad of cotton is placed on top of the column and the excess water is poured out of the funnel by tilting. The column is washed with 5 ml. of 10% pyridine and is ready for use. If the amino acid solution is not added without delay the column must be kept under liquid.

Hydrolysis

A sample of protein, containing 2 to 15 mgm. of lysine, is refluxed with 10 ml. of 6 *N* hydrochloric acid for 24 hr. The hydrolysate is evaporated *in vacuo* to dryness. The residue is taken up in exactly 10 ml. of 10% pyridine and the suspension filtered.

Adsorption

One millilitre of the amino acid solution containing 0.3 to 1.5 mgm. of lysine is passed through the column until a depth of about 1 mm. of solution remains above the surface of the adsorbent and three 1 ml. aliquots of 10% pyridine are added successively to wash all the lysine into the Decalso. The column is then washed with an additional 100 ml. of 10% pyridine and the pyridine washed out of the column with 4 ml. distilled water. The filtrates are discarded and the lysine and arginine eluted with 20 ml. 0.2 *M* sodium carbonate solution, the eluate being collected in a 50 ml. volumetric flask. A small piece of indicator paper is added to the contents of the flask, the hydrogen ion concentration adjusted to pH 3 to 4 with 2 *N* hydrochloric acid, and the solution finally diluted to volume with distilled water.

Chlorination and Colorimetry

A 1 ml. aliquot of the lysine solution containing 5 to 30 μgm. of lysine is carefully measured into a 10 ml. graduated glass-stoppered Pyrex cylinder and 1 ml. of the chlorine solution is added. After allowing to stand for five minutes, 1 ml. of the sodium arsenite solution is added. The mixed alkali solution is then added from a microburette in amount sufficient to adjust the solution to pH 6.2 to 6.5; usually 1.5 ml. is required. The solution is diluted to 9 ml. with distilled water, mixed, and the cylinder placed in a water bath at a temperature of at least 90° C. but not boiling. After a few minutes, 1 ml. of the phenol reagent is added from a slow delivery pipette (about 1 ml. in 15 sec.), the liquid being allowed to flow down the wall of the cylinder. The heating is continued for 40 min. and the solution cooled to room temperature. It is important that the phenol reagent be added in the manner indicated, without removing the cylinder from the bath and without mechanical mixing.

The color intensity is measured with an Evelyn photoelectric colorimeter using a 660 mμ filter. A reagent blank, prepared by carrying out the chlorination and colorimetry with the reagents alone, is used to obtain the 'centre setting' of the colorimeter prior to reading the test solution. The lysine content of the solution may be obtained by reference to a calibration curve (Fig. 2) prepared from readings obtained with standard solutions of *l*(+)-lysine monohydrochloride, A.P. grade (Amino Acid Manufacturers, University of California at Los Angeles), containing 0.5 to 3 mgm. lysine per 100 ml., which had been carried through the procedure, including adsorption on Decalso. The most reliable procedure is to carry out simultaneously a control determination with a standard solution containing approximately the same amount of lysine as that contained in the protein hydrolysate. From the reading with the standard solution, Beer's law constant, K, is calculated from the relation $K = \frac{2 - \log G}{C}$, where C is the concentration of lysine in micrograms per millilitre of standard solution and G is the galvanometer reading. The intensity of the blue color obeys Beer's law over a range of concentrations of 1 to 3 μgm. of lysine per ml. but deviates slightly at lower concentrations.

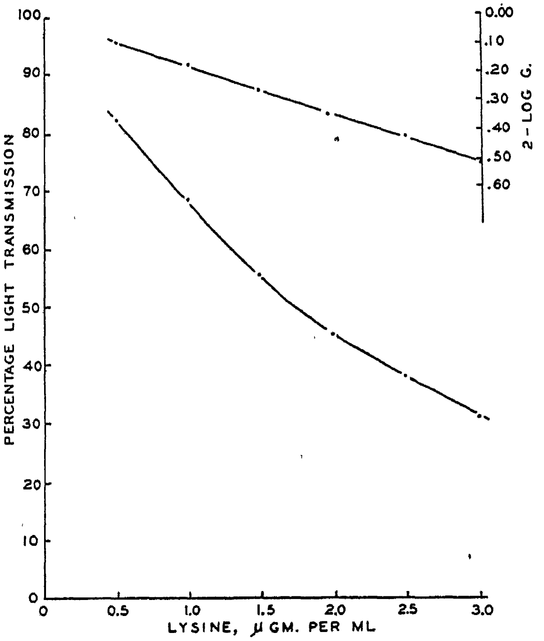

FIG. 2. *Calibration curve and application of Beer's law,* $K = 0.167 \pm 0.003$.

Application of the Method

Satisfactory recoveries of added lysine from a mixture of pure amino acids and from a gelatin hydrolysate have been obtained; the results are presented in Table I. The lysine content of a number of isolated proteins, as determined by the colorimetric method, is given in Table II.

The sample of casein was prepared according to Cohn and Hendry (4). The lysine content, as determined by the colorimetric method, is slightly higher than the values recorded in the literature for the lysine content of casein as determined by isolation procedures. Vickery and White (18) isolated 6.25% lysine from casein; Plimmer and Lowndes (13), 6.13%; Block, Jones, and Gersdorff (3), 6.50%; Ayre (1), 6.09%; Beach *et al.* (2), 6.20%; and Tristram (16), 6.44%. These workers had at their disposal all

TABLE I

RECOVERIES OF ADDED LYSINE FROM A SOLUTION OF PURE AMINO ACIDS AND FROM A GELATIN HYDROLYSATE

Sample analyzed	Total lysine, mgm.		% Recovery of added lysine
	Added	Determined	
Amino acid mixture[1]	4.00	4.05	101.2
" " "	4.00	4.10	102.5
0.1754 gm. gelatin	—	8.47	—
0.3847 gm. "	—	18.25	—
0.3680 gm. "	8.00	25.50	99.1
0.1324 gm. "	12.58	18.64	98.2

[1] *The mixture was composed of 10 mgm. histidine monohydrochloride and 5 mgm. each of glycine, hydroxyproline, leucine, serine, aspartic acid, glutamic acid, proline, alanine, phenylalanine, valine, tyrosine, norleucine, arginine, methionine, cystine, and threonine.*

TABLE II

LYSINE CONTENT OF PROTEINS AS DETERMINED BY THE COLORIMETRIC METHOD

Material	Sample weight for lysine determination, gm.	Ash[1]	Nitrogen[2]	Lysine[2]
Casein	0.0730	1.50	15.36	7.16
	0.0716			7.14
Lactalbumin	0.0726	0.65	15.02	9.12
	0.0581			9.16
Edestin	0.4120	1.32	18.45	2.71
	0.2779			2.78
Gelatin I	0.1754	1.44	17.76	5.41
	0.3843			5.33
Gelatin II	0.5969	Nil	17.52	5.30
Crystalline serum albumin (bovine)	0.0708	—	16.10	12.43
	0.0609	—	—	12.45
	0.0889	—	—	12.46

[1] *Percentage of moisture-free sample.*

[2] *Percentage of moisture and ash-free sample.*

the advantages of improved procedures and data regarding the numerous losses due to the slight solubility of the various compounds.

However, our value is lower than that obtained by Dunn *et al.* (5), employing their microbiological method, and by Zittle and Eldred (19) and Neuberger (11) employing the decarboxylase method. On a comparable basis (corrected for ash and volatile matter) their values are 8.30, 7.8, and 7.5%, respectively, whereas our average value is 7.15% lysine. Collaborative studies on the determination of lysine by the microbiological, enzymic, colorimetric, and classical methods should be conducted on the same sample of the highest obtainable degree of purity, to arrive at a generally acceptable value for the lysine content of casein. The possibility that the lysine content of casein preparations is variable, as has been suggested in the case of tryptophane (14), should also be investigated.

The lactalbumin was prepared by the method outlined by Plimmer and Lowndes (13). The other proteins were commercial preparations, i.e., edestin (Eimer and Amend) and gelatin (Baker and Adamson). The second sample of gelatin was purified according to the procedure of Loeb (8, pp. 34-36) for ash-free gelatin. The values for the lysine content of these proteins, as determined by the colorimetric method (Table II) are in good agreement with the values reported in the literature and obtained by isolation procedures (12, 13, 15, 17). The crystalline bovine serum albumin was from the same sample analyzed by Shemin (15) by the isotope dilution method, and it was found to contain 12.42% lysine.

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THE THERMAL EXPLOSION OF LEAD AZIDE[1]

By A. S. Hawkes[2] and C. A. Winkler[3]

Abstract

The minimum explosion temperatures for service and dextrin azides (about 315° C. and 275° C., respectively) are increased considerably by increase of surface:volume ratio of the container and by compressing or wetting the charge with dibutyl phthalate before explosion. When wetted, the two azides were found to be similar in respect of minimum explosion temperatures and induction periods prior to explosion. Sensitization of service azide by preheating was found to be permanent. A limit to sensitization below the minimum explosion temperature was observed, and probably exists also for sensitization above this temperature. Wetting the charge with phthalate nullifies the sensitization. Although dextrin azide alone is more thermally sensitive than service azide, mixtures of the two containing 70% or more service azide show a sharp change to service azide properties; the mixtures apparently are not exploded by the dextrin azide they contain. The value of E in the expression $\ln t = \frac{E}{RT} +$ constant, where t is the induction period, has been determined for both the initial and final stages of reaction preceding explosion and found to be essentially unaltered. Minimum explosion temperature of single large crystals was shown to increase with crystal size. The data are interpreted as showing that the thermal explosion of lead azide may result from self-heating, the heat of the pre-explosion reaction not being sufficiently dissipated from the material.

Introduction

The thermal explosion of pure lead azide has been found (1, 8, 19) to have three characteristics of particular interest. (i) There is an induction period, followed by rapid reaction which may or may not lead to explosion, depending on the temperature. (ii) Spontaneous or self-heating of the solid occurs during the decomposition (1, 19). (iii) Samples of pure azide that have been heated and quenched by chilling before explosion occurs require a shorter period of heating a second time to produce explosion (19). Such samples have been termed 'sensitized'.

In addition to pure ('service') azide there is a material also prepared that is precipitated in the presence of dextrin ('dextrin azide'). Service and dextrin azide are crystallographically identical by X-ray examination, but, whereas service azide crystals are generally whole or twinned, the dextrin grains consist of agglomerates of minute crystallites. The two types have been found (19) to differ considerably in their behavior to thermal decomposition. Dextrin azide is capable of explosion at about 275° C., some 40° C. lower than service azide, and, while service azide at suitably chosen temperatures may exhibit induction periods of over a minute, the dextrin material generally shows

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[2] *Chemist, Trinidad Leaseholds Limited, Pointe à Pierre, Trinidad. At the time, holder of a Studentship under the National Research Council of Canada.*

[3] *Professor of Chemistry.*

induction periods of not more than 12 to 14 sec. From the effect of temperature on the induction period and application of the relation $\ln t = \frac{E}{RT} + \text{constant}$, where t is the induction period, and E is the activation energy, values of E of 41.3 and 23.4 kcal. for service and dextrin azides respectively were obtained (19). The difference was accounted for on the basis of a greater number of active centres on the larger available surface of the dextrin azide. Data to be presented later indicate that values of E so obtained should not be interpreted in the sense of a true activation energy for the reaction leading to explosion of lead azides.

Studies on explosions in solids such as the azides of the alkali and alkaline earth metals, as well as lead azide, mercury fulminate, and others, have resulted in dissimilar views about the mechanism whereby explosion is initiated and propagated in such systems (2-12, 14-18). Probably the diversity of opinions merely reflects an inadequate and too flexible experimental background. It was mainly with a view to supplementing the comparatively meagre experimental data that the present study was made.

Experimental and Results

Apparatus

A. *Bulk Detonation*

For experiments with bulk material, the apparatus was similar to that used by Ubbelohde (19). The heating bath consisted of an electrically heated block into which was drilled a hole to contain melted tin as the thermostat fluid. Temperature was controlled manually and measured by a sheathed chromel–alumel thermocouple in the melted tin. For most of the experiments, 20-mgm. samples of azide were weighed into No. 8 blasting caps, the bottoms of which had been rounded on a steel jig to ensure uniform distribution of the charge from sample to sample. A small hole through each cap about 1 cm. from the top permitted the cap to be wired to a holder that could be manipulated in suitable guides from behind a safety screen. In this way, samples could be introduced into the thermostat, or removed from it for quenching in ice-water, in a rapid reproducible manner. Heating times were determined with a stop watch.

B. *Single Crystals*

The behavior of single, large crystals of azide was studied in a furnace made from a short length of 2 mm. bore Pyrex capillary, into one side of which was blown a small hole to admit a platinum–rhodium thermocouple. The electrically heated furnace was mounted in the hole of a microscope stage, the objective lens of the microscope being cooled by a film of water to prevent damage to it. The azide crystal was thrust into the furnace by placing it on a small glass rod ground to semicircular cross section. A thin Pyrex thread fused at one end to the rod acted as a spring under which the crystal could be placed and held securely in position. A micrometer eyepiece in the microscope permitted crystal dimensions to be measured. As before, heating times were determined with a stop watch.

Materials

Service and dextrin azides were obtained through the courtesy of Canadian Industries Limited. The service material was white, and showed little crystal twinning. The rather fluffy dextrin azide was light yellow, the grains appearing under the microscope as agglomerates.

Large crystals of service azide were made by the method of Miles (13). Many of the crystals so prepared were 3 to 4 mm. long, but were relatively insensitive, not exploding when crushed or broken.

Precision of Measurement

The precision with which the induction period (i.e., time to explosion) could be measured was determined using 20-mgm. samples. For dextrin azide the maximum deviation from the mean value was 5% at 280° C. and 8% at 295° C., while with service azide the deviation rarely exceeded 5% at any temperatures used. Cooling of the thermostat (about 0.5° C.) during the induction period was probably responsible for most of the observed variability, though timing, size of sample, variations in crystal size between samples, and distribution of charge in the tube also contributed to fluctuations in observed induction periods. For example, 10 mgm. dextrin azide in the tube at 295° C. gave an average induction period of 5.4 sec., while with 20-mgm. samples at the same temperature the value was 7.6 sec.

Minimum Explosion Temperature

In blasting caps, a well defined minimum temperature was found to exist, below which explosion of lead azide would not occur, even after prolonged heating, but above which explosion occurred at every trial. For a given batch of azide this minimum temperature was critical within 0.5° to 1° C., but varied as much as 6° C. with different batches of dextrin azide. The value for dextrin azide was generally found to be 270° to 273° C., that for service azide 314° to 315.5° C., when the samples were exploded in the No. 8 blasting caps. It was found, however, that these minimum explosion temperatures could be altered rather drastically by change of the surface:volume ratio of the tube containing the material. For example, with dextrin azide, a minimum explosion temperature of 272° C. in No. 8 blasting caps was increased to 310° to 317° C. in sufficiently small bore glass capillary tubes, while with service azide a change from 314° to 323° C. was readily produced in similar manner.

The minimum explosion temperatures of both types of azide were also found to increase appreciably if the materials were packed by pressure after being introduced into the blasting caps instead of being simply poured into the caps. The increase with dextrin azide was 5° C. while that with service azide was 15° C. with the degree of packing used in the experiments.

The addition of a few drops (approximately 42 mgm.) of dibutyl phthalate to the azide contained in blasting caps also increased the minimum explosion temperatures over those for untreated materials, the increases noted being approximately 7° and 40° C. for service and dextrin azides respectively. Simultaneously with the marked change in minimum explosion temperature of dextrin azide when treated with dibutyl phthalate there was an increase in the induction period prior to explosion to a value comparable with that for service azide (approximately 86 sec.). In fact, the effect of both packing and wetting with phthalate was generally to make the behavior of dextrin azide resemble more closely that of service azide.

Effect of Temperature on the Induction Period

The effect of temperature on the induction periods of service and dextrin azides in No. 8 caps is given in Table I.

TABLE I

EFFECT OF TEMPERATURE ON INDUCTION PERIODS OF DRY AZIDES

Service azide		Dextrin azide	
Temp., ° C.	Induction period, sec.[1]	Temp., ° C.	Induction period, sec.[1]
320	48.8	277	11.6
325	30.8	280	10.3
335	14.5	285	8.9
345	8.7	305	6.6
355	5.6	325	5.3
365	4.0	345	3.8
375	2.6	365	2.9

[1] *Average of at least four determinations.*

A similar series of experiments was made using azides wetted with dibutyl phthalate. The effect of temperature is then given by the data in Table II.

TABLE II

EFFECT OF TEMPERATURE ON INDUCTION PERIODS OF AZIDES WETTED WITH DIBUTYL PHTHALATE

Service azide		Dextrin azide	
Temp., ° C.	Induction period, sec.[1]	Temp., ° C.	Induction period, sec.[1]
325	59.8	330	60.2
345	29.4	335	31.0
355	5.8	345	9.0
360	2.8	355	4.0
		365	1.9

[1] *Average of at least four determinations.*

Representing the induction period by t, a plot of log t against $\frac{1}{T}$ gives the curves in Fig. 1. It will be noted that the relation for service azide is nearly linear when the material is wetted by phthalate and that wetting has again made the behavior of the two types of azide essentially the same. From the relation

$$\ln t = \frac{E}{RT} + B$$

values of E may be calculated. For dry dextrin azide the value obtained is 10.6 kcal., while with dry service azide it varies from 31 kcal. at the highest temperatures used to 65 kcal. at the lowest. Calculations for the wetted azides, however, give values of 87 and 97 kcal. for service and dextrin azides, respectively, at the lowest temperatures, while at the highest temperatures used the corresponding E values are 66 and 60 kcal. It is of interest, perhaps, that the values of E for wetted materials do reflect the identical chemical composition of dextrin and service azides, but it is probable that values of E obtained in this way do not represent true activation energies for the reaction leading to explosion, since they are so dependent upon purely physical characteristics of the system. The reasons for this dependence will become clear later.

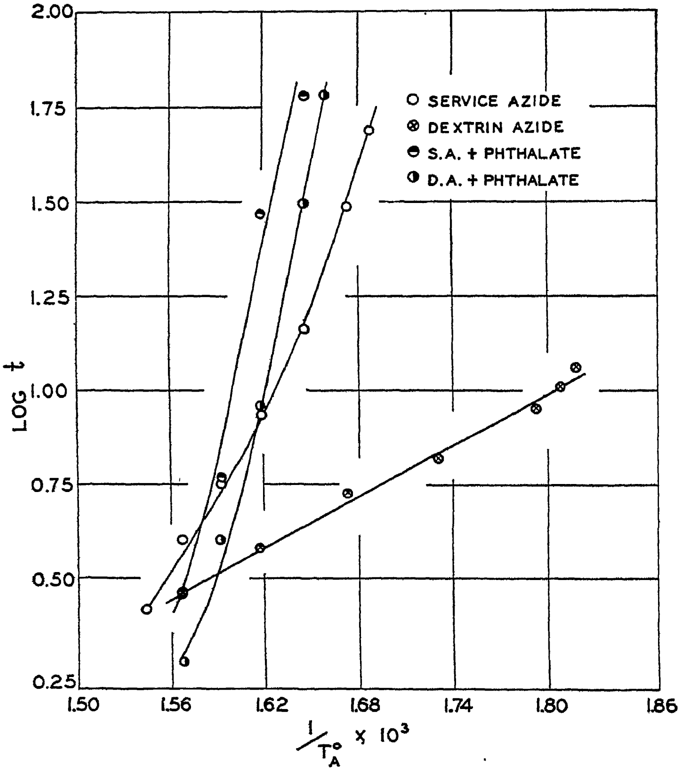

FIG. 1. *Plot of log t—* $\frac{1}{T}$ *relations for dry and phthalate wetted azides.*

Sensitization by Preheating

Service azide is readily sensitized in the Ubbelohde sense (19); that is, if a sample is heated at a given temperature for a fraction of the full induction period, and the pre-explosion reaction quickly quenched, for example, by plunging the container into ice-water, a second heating period culminating in explosion is shorter than the single induction period at that temperature. The extent of sensitization depends on the time and temperature of preheating. Typical sensitization data obtained in the present study are recorded in Table III, where t_1 = preheating time, t_2 = second heating time for explosion, T = temperature during both heating periods, and t = time for explosion by a single heating period at the same temperature. It will be noted that t_2 was always less than t by an amount that depended on t_1, and that $(t_1 + t_2)$ was always larger than t. It is of interest that the azide may be preheated to within one or two seconds of explosion, yet require a considerable second heating period, t_2, after quenching to produce explosion. This would suggest that most of the reaction culminating in explosion occurs in a very short time immediately preceding explosion, and that if the rate of the pre-explosion reaction is appreciably influenced by self-catalysis, practically all the catalytic products are produced immediately prior to explosion.

TABLE III

SENSITIZATION OF SERVICE AZIDE

$T = 320°$ C. $t = 47.0$ sec.		$T = 330°$ C. $t = 20.3$ sec.	
t_1, sec.	t_2, sec.	t_1, sec.	t_2, sec.
15	34.8	5	18.3
25	24.8	8	16.4
30	24.8	10	14.6
35	22.8	15	12.3
43	22.2	18	11.7
45	Exploded on withdrawal	19	10.3
		20	Exploded on withdrawal

There is a limit to the sensitization possible by preheating. This limit was observed and studied by preheating at temperatures below the minimum explosion temperature so that long preheating periods without explosion were possible. After the preheating treatment, the material was quenched, then brought to explosion at a temperature above the minimum explosion value. The length of the second heating period gives a measure of the degree of sensitization. The data are shown in Table IV, where T_1 = preheating temperature, t_1 = preheating time, T_2 = second heating temperature, and t_2 = second heating time culminating in explosion at T_2.

TABLE IV

SENSITIZATION OF SERVICE AZIDE BY PREHEATING BELOW THE MINIMUM EXPLOSION TEMPERATURE

T_1 = 310° C. T_2 = 320° C.

t_1, sec.	20	30	40	50	60	70	80	90	100	120	150
Av. t_2, sec.[1]	38.4	31.4	26.5	23.6	23.6	22.2	21.4	19.9	19.7	18.8	20.3

t_1, sec.	175	200
Av. t_2, sec.[1]	24.4	No explosion

[1] *Average of at least four determinations.*

From the table it is evident that the maximum sensitization corresponded to a reduction in t_2 to about 19 sec. from a normal induction period at 320° C., for a single heating of about 50 sec. Prolonged preheating apparently raised the minimum explosion temperature above 320° C.

Careful re-examination of the sensitization at 320° C. (cf. Table III), with explosion also at 320° C., gave no indication of a limiting sensitization being reached, and the minimum explosion temperature remained essentially unaltered. Hence, material sensitized to the maximum extent without explosion occurring above the minimum explosion temperature would seem to be in a different condition than material whose minimum explosion temperature had been seriously altered by prolonged sensitization below the minimum explosion temperature. Examination of normal, partially sensitized, and fully sensitized azide samples by X-ray diffraction gave no evidence of alteration in the sensitized materials.

No successful sensitization of dry dextrin azide above its minimum explosion temperature was found possible. By preheating slightly below the minimum explosion temperature, the data shown in Table V were obtained. The induction period for a single heating at 280° C. was 9.0 sec. for the batch used. It may be reasonably doubted that the data correspond to true sensitization of the material.

TABLE V

SENSITIZATION OF DRY DEXTRIN AZIDE

T_1 = 275° C. T_2 = 280° C.

t_1, sec.	10	7	5	3	3	2	2	1	1
Av. t_2, sec.	No explosion	10.6	10.4	8.0	8.4	8.1	8.1	8.2	8.2

While sensitization of the dextrin material was slight, desensitization was readily accomplished, corresponding to an increase of the minimum explosion temperature from its normal value of 276° C. to a value above 280° C.

Sensitization of dextrin azide was greatly facilitated by wetting with dibutyl phthalate. For a batch that showed, when wetted, an induction period for single heating at 335° C. of 41 sec., it was found that preheating four wetted samples at 335° C. for 25 sec. resulted in explosion on a second heating after 21.0, 17.9, 18.0, and 23.8 sec. for the four samples. Again, wetted dextrin azide behaved similarly to service azide.

Duration of the Sensitization

Duration of sensitization in service azide was studied by preheating four series of samples for 20 sec. at 320° C., and storing them at room temperature under the following conditions.

Series *A*: In dark, over concentrated sulphuric acid.
Series *B*: In dark, in nitrogen, over concentrated sulphuric acid.
Series *C*: In dark, over water.
Series *D*: Exposed to diffuse light, over water.

Samples were removed periodically and the time of second heating to explosion was measured. The total storage times were 1122 hr. for Series *A*, 1051 hr. for Series *B*, 790 hr. for Series *C*, and 404 hr. for Series *D*.

In general, there was considerable variability in the times of second heating to explosion, but with only a few of the samples, among those stored over water, was it impossible to bring about explosion at 320° C. The sensitization effect was essentially unaltered with most of the samples. Those that failed to explode at 320° C. after storage suffered a 6° to 7° C. increase in minimum explosion temperature during storage, to a value of 322° C. This increase in minimum explosion temperature in samples stored over water could be attributed to the fact that, on storage, the azide in such samples tended to bind together, to become lumpy and no longer free-flowing. The data indicated clearly that, over a period of approximately three months, the sensitization was retained essentially unaltered.

A further indication that the sensitization effect was not readily eliminated, even at higher temperatures, was obtained in experiments in which, instead of rapidly quenching the sensitized material in ice-water, it was allowed to cool comparatively slowly. This was done by preheating the samples at 310° C., after which they were raised so that the bottom of the charge container was just above the level of the thermostat fluid for 30 sec., then raised again until the bottom of the container was about 1 in. below the top of the steel heating block, for another 30 sec., then cooled in air for five minutes, during the first minute of which the container was held about 2 in. directly above the block. No ice-water was used to quench the samples. The azide was finally exploded at 320° C. Six samples treated in this way failed to show any significant effect of the rate of cooling on the extent of sensitization by the preheating treatment.

Effect of Phthalate on Sensitized Service Azide

If sensitization of service azide by preheating produces a distinct chemical change in the crystals, it would hardly be expected that wetting sensitized samples with dibutyl phthalate should obliterate the sensitization. However, when service azide was sensitized to the maximum extent above and below the minimum explosion temperature, then exploded at 335° C. in the presence of added phthalate, the data of Table VI were obtained. Unsensitized samples similarly wetted with phthalate and exploded by a single heating showed an induction period of 37.3 sec. (average) at the same temperature.

TABLE VI

EFFECT OF PHTHALATE ON SENSITIZED SERVICE AZIDE

Time of sensitization, sec.	Time of second heating, sec.[1]
A. Temperature of sensitization = 310° C.	
100	39.9
120	42.2
150	39.9
B. Temperature of sensitization = 320° C.	
42	40.8

[1] *Average of at least three determinations.*

From previous data, preheating for 120 sec. at 310° C. corresponds to maximum sensitization, while samples heated at 310° C. for 150 sec. should have second heating times longer than those preheated for 120 sec. However, the addition of phthalate has eliminated all the sensitizing effect of preheating, regardless of whether the preheating treatment was above or below that for maximum effect, or whether the sensitization was induced above or below the minimum explosion temperature. The effect of phthalate addition to sensitized service azide would seem to be entirely similar to the effect of adding phthalate to dextrin azide, from which it seems logical to suggest that sensitization of service azide should be explicable on the same basis as the difference in behavior of dextrin and service azides.

Explosion of Mixtures of Service and Dextrin Azides

Since service and dextrin azides differ markedly in their thermal explosion properties, it was of interest to examine the induction periods of mixtures of the two types. Mixtures containing various proportions of the two azides were made and 20-mgm. samples of each mixture exploded at 320° C. The minimum explosion temperature of each mixture was also determined. The results are plotted in Fig. 2.

The data indicate that the properties of the mixtures are sensitive to small changes in the ratios of the components. The plot of *t* vs. composition is discontinuous at 75% service azide because of an increase in minimum explosion temperature to 321° C. for that composition, while the explosion temperature used throughout was 320° C. The discontinuity would widen at the lower, and disappear for a sufficiently high, temperature of explosion. It is also interesting to note that the discontinuity occurs at percentages of service azide slightly above a range of compositions where the induction periods are closely similar to those of dextrin azide itself, despite the fact that such mixtures may contain as much as 70% service azide.

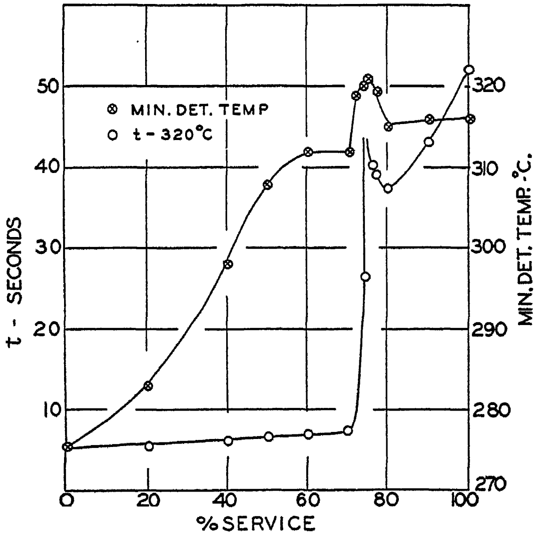

FIG. 2. *Induction periods and minimum explosion temperatures of service-dextrin azide mixtures.*

The effect of temperature on explosion of the various mixtures was also determined. A plot of log *t* against $\frac{1}{T}$, as in Fig. 3, shows an abrupt change in explosion characteristics of the mixtures at lower temperatures.

The abrupt change in explosion behavior at 75% service azide is accompanied by a maximum in the packing density at the same composition. The relative packing densities of different mixtures were measured by successively weighing 50-mgm. samples of each mixture into a fine bore capillary tube, the tube being tapped and rubbed with a file until three successive measurements of the height of any given sample in the tube gave concordant values. The reciprocal of the relative heights for different mixtures in the same tube gave a measure of the relative packing densities. The data obtained are recorded in Table VII.

It is evident that mixtures of composition in the neighborhood of 75% service azide pack to higher density than mixtures of other compositions.

Explosion of Mixtures of Sensitized and Normal Service Azide

Sensitized service azide resembles dextrin azide in that it has a fairly short induction period. Explosion of mixtures made up of sensitized and normal service azides should give information on whether the effect of dextrin azide in service–dextrin mixtures is the result of its shorter induction period or of some other factor.

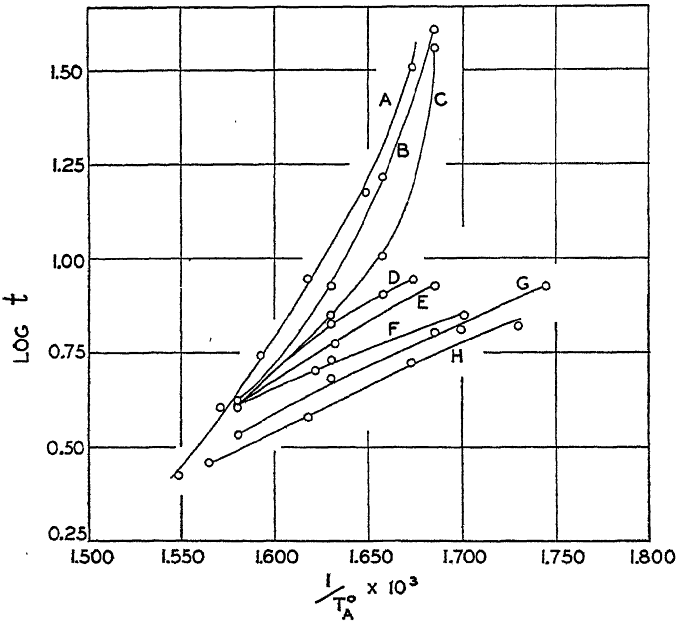

FIG. 3. *Variation of induction periods with temperature for service–dextrin azide mixtures.*

A = 100% service azide
B = 90% " "
C = 80% " "
D = 75% " "
E = 70% service azide
F = 60% " "
G = 30% " "
H = 100% dextrin azide

TABLE VII

RELATIVE PACKING DENSITIES OF SERVICE–DEXTRIN AZIDE MIXTURES

Service azide, %	Height in tube, mm.[1]
0	117.9
70	101.4
75	99.3
80	99.8
100	103.7

[1] *Each value the average of four determinations.*

Service azide was sensitized in 20-mgm. quantities by heating at 320° C. (above minimum explosion temperature) for 25 sec. Mixtures of this sensitized material with unsensitized service azide were made to various compositions and exploded in 20-mgm. quantities at 320° C. The minimum explosion temperatures were also determined. The data, plotted in Fig. 4, show a fairly steady increase in induction period with increased content of normal azide, and a slight maximum in the minimum explosion temperature between 20 and 30% content of untreated azide. At no composition is there any indication of a sharp break in either curve. It may be inferred then that the unusual curves obtained with service–dextrin azide mixtures are due to factors other than the short induction period of dextrin azide.

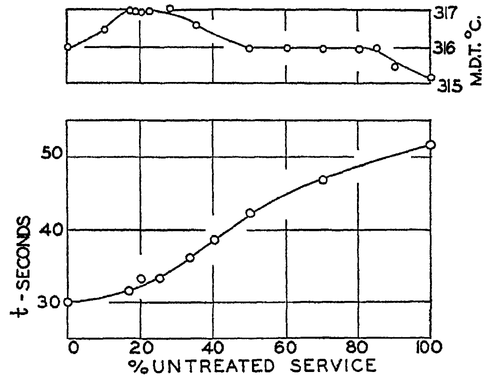

FIG. 4. *Induction periods and minimum explosion temperatures of mixtures of normal and sensitized service azides at 320° C.*

From previous experience it was anticipated that the sharp increase in induction period of service–dextrin mixtures in the region of 70 to 80% service azide would be reduced, if not eliminated, by wetting the mixtures with dibutyl phthalate. Accordingly, 20-mgm. samples of mixtures containing 30, 75, and 80% service azide were wetted with phthalate and exploded at 340° C., the average induction periods being 27.3, 34.2, and 32.3 sec. respectively. Evidently the spread between induction periods for mixtures below and above 70% service azide (cf. Fig. 2) was markedly reduced by wetting with phthalate.

Values of E for Initial and Final Stages of the Induction Period

If, during the induction period, there is first a reaction responsible for sensitization (sensitization reaction) which is fundamentally different from a later reaction culminating in explosion (explosion reaction), it would be expected that values of E for the initial and final stages of the induction period should be significantly different. The sensitization reaction, for example, might be assumed to form nuclei of some kind which serve to catalyze the explosion reaction.

The value of E for the first part of the induction period (sensitization reaction) was determined by heating service azide for the required times at different temperatures to produce essentially constant degree of sensitization in the material. In practice, the temperature and time of sensitization t were adjusted to give an induction period on the second heating of 24 ± 0.5 sec. at 320° C. The data obtained are given in Table VIII. The value of 51 sec. at 310° C. is interpolated from Table IV, while the experimentally unattainable value of 11 sec. at 340° C. is estimated from the observations that the induction period for a single heating at 340° C. was 11.5 sec., while preheating up to 10 sec. at 340° C. reduced the second heating period for explosion at 320° C. to 29.2 sec. (from a single heating induction period of 49 sec.).

TABLE VIII

DATA FOR EVALUATING E FOR THE SENSITIZATION REACTION (SERVICE AZIDE)

Temperature, ° C.	Time of sensitization, sec.
300	100
310	51
320	35
330	20
340	11

The data in Table VIII are plotted in Fig. 4, from which a value of E of 37 kcal. was evaluated.

The value of E for the explosion of sensitized azide was also measured. For this estimation, samples were preheated for 20 sec. at 320° C., quenched, then exploded by heating at various temperatures. The data are shown in Table IX.

TABLE IX

DATA FOR EVALUATING E FOR EXPLOSION OF SENSITIZED SERVICE AZIDE

Explosion temp., ° C.	Time for explosion, sec.[1]
320	29.7
330	16.6
340	8.5
350	5.7
365	3.4
375	2.1

[1] *Each value the average of at least six determinations.*

These data are also plotted in Fig. 5, and yield an E value of 41 kcal.

The values of E for sensitization and explosion agree sufficiently well to suggest that there is no difference between the two reactions. It would seem improbable, for example, that one reaction (sensitization) produced a catalyst for the other (explosion).

Experiments with Single Crystals

The principal factor governing the minimum explosion temperature of single lead azide crystals was found to be their size, the larger particles exploding at lower temperatures. Some examples of the effect are given in Table X. The dimensions are in divisions of the eyepiece micrometer scale (1 mm. = 65 divisions), and are recorded in order of length, thickness (height), and width

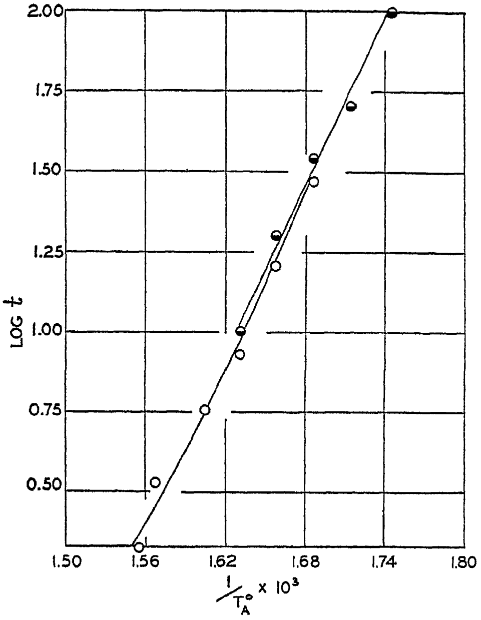

FIG. 5. *Effect of temperature on time of preheating service azide to a given degree of sensitization (upper curve) and on time for explosion of sensitized service azide (lower curve).*

TABLE X

EFFECT OF CRYSTAL SIZE ON MINIMUM EXPLOSION TEMPERATURE OF SINGLE CRYSTALS

Crystal size, mic. div.	Temp., ° C.	Cross-sectional area, (mic. div.)^2	Remarks
43 by 8 by 14	320	112	No explosion
53 by 13 by 10	320	130	" "
53 by 18 by 15	320	270	Broke—25 sec.
44 by 8 by 14	325	112	No explosion
49 by 16 by 16	325	256	Broke—22 sec.
66 by 9 by 14	332	126	No explosion
61 by 18 by 15	332	270	Broke—15 sec.
39 by 9 by 14	340	126	No explosion
50 by 8 by 18	340	144	Broke—17 sec.
52 by 10 by 16	340	160	" —17 sec.
49 by 13 by 17	340	221	" —18 sec.
58 by 8 by 17	347	136	" —13 sec.

of the crystal. The explosion was incomplete at lower temperatures (below about 350° C.), but the crystal broke up abruptly, accompanied by a faint crackling sound. The time lag preceding the crystal fracture was taken as the induction period preceding the partial explosion.

It will be noted from Table X that the cross section of the crystal is the important factor in relation to its explosion characteristics.

Activation Energy for Explosion in Single Crystals

A value of E for the explosion of single crystals was obtained by exploding single crystals, of approximately the same size, over a range of temperatures, and timing their induction periods to the nearest second. The data, given in Table XI, correspond to a value of E of approximately 10 kcal. This value is much smaller than that for explosion of bulk service azide, but is almost identical with that for dextrin azide.

TABLE XI

EFFECT OF TEMPERATURE ON THE INDUCTION PERIOD FOR SINGLE CRYSTALS

Temp., ° C.	Crystal size, div.	t, sec.
320	56 by 17 by 20	18
320	59 by 11 by 18	19
334	62 by 15 by 18	16
334	57 by 18 by 20	15
348	61 by 22 by 20	13
348	70 by 20 by 16	12
390	70 by 18 by 23	7
390	70 by 14 by 20	8

Sensitization of Single Crystals

Attempts were made to sensitize single crystals of service azide by preheating, the reaction being quenched by quickly withdrawing the crystal from the furnace and cooling it in an air stream. There was some indication of sensitization, corresponding to a possible reduction of the second heating period from 18 to 16 sec., but reasonable doubt can be entertained of its reality. After the preheating treatment the crystals showed darkening at the ends and, in more advanced stages of treatment, also along the edges or wherever roughness was visible. Crystals heated to within one to two seconds of explosion, then quenched, were by no means covered with the dark brown deposit, and on breaking the crystals it was evident that the deposits were on the outer faces only and, at that stage of reaction at least, had not begun to penetrate into the interior.

Self-heating of Single Crystals

With single crystals, it was possible to predict explosion a second or two before it occurred by noting the time at which an apparently abrupt swelling of the crystal occurred (viewed through a micrometer eyepiece). This swelling was probably a manifestation of self-heating within the crystal. With about 10% of the samples studied, the swelling was reflected in a noticeable increase in length, the magnitude of which was ascertained as approximately 0.6 scale division for a crystal about 60 divisions long. The approximate coefficient of thermal expansion of service azide was estimated by making many measurements of crystal lengths at room temperature and at 310° C. (below the explosion temperature). The crystals were found to expand about 0.4 micrometer division over this temperature range for a crystal length of approximately 60 divisions. If the coefficient of linear expansion is reasonably constant between room temperature and explosion, it is readily estimated that the crystal temperature (as distinct from the furnace temperature) immediately prior to explosion was of the order of 750° C.

Discussion

The results of the present investigation would seem to be adequately explained by merely assuming that self-heating of lead azide, resulting from inefficient dissipation of the heat of decomposition, accelerates the reaction to one of explosive violence. This view is in contrast to others which assume the process to depend on the probability of chains (energy or material) colliding, the probability of simultaneous decomposition of adjacent molecules, or other similar coincidences, to produce sufficiently localized concentrations of energy to bring about explosion. These probability theories are based largely on past observations that the induction periods leading to explosion were variable at constant temperature, whereas the present study indicates that with attention to temperature control, ratio of surface to volume of container, etc., the precision with which the induction periods can be measured is within a reasonable 5% limit.

The present view is also to be contrasted with others which assume the initial formation of catalytic nuclei. The observation recorded earlier that the value of E for the sensitization reaction is essentially the same as that for the explosion of sensitized azide does not suggest that the explosion is catalyzed to any large extent by the products of the sensitization reaction.

The suggestion that the thermal conductivity of the system is a principal factor in the initiation of lead azide seems to provide a ready interpretation of all the observations recorded during the present study. In discussing the behavior under various conditions, clear distinction must be made between temperature of the thermostat and actual temperature within the azide mass and azide crystals.

The lower minimum explosion temperature for dextrin azide, and its shorter induction period, relative to service azide, are accounted for immediately on the plausible assumption that the intercrystal thermal conductivity of service azide is greater than the conductivity between agglomerates in dextrin azide. In such an event, the self-heating in dextrin azide should be more marked than in service azide, and explosion of dextrin azide therefore occurs at a lower thermostat temperature (but not lower azide temperature), and in shorter time. Similarly, the increase of minimum explosion temperature with increased surface of material in contact with the wall of the sample container may be attributed to greater loss of heat from the sample to the thermostat, so that the thermostat must be maintained at a higher temperature for the explosion temperature to be attained by self-heating within the azide mass. Compression of the charges, which should improve thermal contact between the particles, should, by this argument, also result in increased minimum explosion temperature (thermostat) and such an effect was observed. Likewise, wetting with phthalate, to establish better thermal contact between particles, brought about an anticipated increase in minimum thermostat temperature necessary for explosion. The argument is equally applicable to the behavior of service–dextrin mixtures, where the mixture of maximum packing density, with unquestionably the best thermal conductivity, required the highest thermostat temperature to bring about explosion. Moreover, there is the interesting observation that with such mixtures the induction period is several times that of the sensitive component, dextrin azide, when the proportion of service azide is sufficiently high. This behavior is readily explained on the basis of improved thermal conductivity of the mixtures containing service azide, and is difficult to explain otherwise. Finally, the work on single crystals where larger crystals, with their undoubtedly smaller rate of heat loss, were found to have lower minimum thermostat temperatures for explosion, gives added credibility to the simple concept of self-heating as the main factor in the initiation of azide explosion.

The nature of the sensitization produced by preheating is largely a matter for speculation. However, most of the data obtained in this investigation can be explained by the simple assumption that roughening of the crystal surfaces during preheating may render contact between crystals less intimate, so that heat produced by self-heating is less readily dissipated to the thermostat. The formation of a lead oxide layer, for example, might produce such an effect.

If sensitization resulted from a change in thermal conductivity as suggested it would be expected, and is observed, that samples preheated to within one or two seconds of explosion should require for explosion a second heating period, not of one or two seconds, but sufficiently long to reproduce by self-heating the internal temperature that existed at the time the sample was quenched. Also, the values of E for the preheating and explosion reactions would be expected, and are found, to be similar, since the nature of the reaction involved would presumably remain unaltered. The durability of the sensitization under the various storage conditions used, the failure to sensitize single crystals, and the observed elimination of sensitization in service azide by wetting with phthalate, all receive ready explanation by the assumption that sensitization is due to a surface effect leading to decreased intercrystal thermal conductivity. However, it is not readily apparent on this basis why wetted, but not dry, dextrin azide should be capable of sensitization, nor can more than a suggestion be offered for the optimum in sensitization reached when samples are preheated below the explosion temperature for prolonged periods. The desensitizing effect of prolonged heating might be due to production of minute fissures in the crystals, thus effectively increasing the surface:volume ratio and increasing the rate of heat loss from the crystals. Such increase in surface: volume ratio should be accompanied by increase in the minimum explosion temperature (on basis of preceding arguments) and such increases, though small, were in fact observed.

With self-heating apparently playing such an important part in the explosion of lead azide it is questionable that the term activation energy should be applied to the quantity E in the expression $\ln t = \frac{E}{RT} + \text{constant}$. The value of E has been shown to depend on purely physical characteristics of the system. This dependence, which is readily understood in terms of changes in ease with which the heat of reaction is dissipated, clearly indicates that a value of E so obtained is not a true measure of the activation energy for the chemical reaction culminating in explosion.

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PRELIMINARY OBSERVATIONS OF THE DIELECTRIC CONSTANTS OF VAPORS ADSORBED ON ACTIVATED SILICA[1]

By R. McIntosh,[2] H. S. Johnson,[3] N. Hollies,[3] and L. McLeod[2]

Abstract

A measure of the dielectric constants of several substances adsorbed on silica gel has been obtained by measuring the change in the capacity of an electrical condenser when measured amounts of the substances were adsorbed on silica gel situated between the plates of the condenser. The substances examined were ethyl chloride, *n*-butane, and ethylene oxide. The plot of capacity change vs. amount adsorbed was found, in all cases, to consist of two or more quite distinct sections, each approximating to linearity. The temperature coefficients of dielectric constant were evaluated. The dielectric constant calculated for adsorbed *n*-butane was close to that calculated for the bulk liquid, whereas the value calculated for adsorbed ethyl chloride was significantly lower than the value calculated for the liquid.

Introduction

Although adsorption theories, such as those of Brunauer, Emmett, and Teller (4), and Jura and Harkins (10) permit of some inferences concerning the nature of adsorbed layers, relatively few of the physical properties of such layers have been studied in a direct way. The present paper describes attempts to obtain a direct measure of the dielectric constant of the adsorbate by measurement of the change in electrical capacity resulting from increments of vapor to an adsorbent between the plates of an electrical condenser. The relation between the experimentally determined capacity changes and the dielectric constant of the adsorbate is not yet completely established, although the problem has attracted the attention of a number of investigators (2). A slight dependence on the crystal form of the solid component, for example, is indicated. However, a linear relation between the change in capacity on the one hand, and the dielectric constants and volumes of the adsorbate and vapor phase on the other, is often used (1, 8) and appears to give good results. If we indicate the solid, adsorbed, and vapor phases respectively by the subscripts 1, 2, and 3, the fraction of the total condenser volume occupied by each by f_1, f_2, and f_3, the dielectric constant of each by e_1, e_2, and e_3, the relation is (12):

$$e = f_1e_1 + f_2e_2 + f_3e_3 \ , \tag{1}$$

where e is the effective dielectric constant of the mixture. An increment of the material being adsorbed produces a change of dielectric constant

$$\triangle e = \triangle f_2e_2 + \triangle f_3e_3 \ , \tag{2}$$

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[2] *Chemist, National Research Laboratories, Ottawa.*

[3] *Graduate Student in Physical Chemistry, McGill University, Montreal, Que. Holder of a Studentship under the National Research Council of Canada.*

assuming f_1e_1 to remain unchanged. Since e_3, the dielectric constant of the vapor, is known, this equation permits the calculation of e_2. All the uncertainties in the use of this equation do not obscure the fact that a plot of $\Delta e - \Delta f_3e_3$ vs. amount adsorbed should be very nearly linear if the dielectric constants of successive portions of adsorbate are the same. In particular, any sharp change of slope in this curve must mean that the two portions of adsorbate corresponding to the two portions of the curve have different dielectric constants. It may be noted here that values of C quoted subsequently include the small correction ($C_0 \, \Delta \, f_3e_3$) for changes in the amount of vapor present. C_0 is the capacity of the condenser when empty.

Interpretation of the results of these measurements, though not free from complication, is capable of giving valuable information concerning the physical state and mobility of the adsorbed molecules. Even more readily detected are *changes* in these properties with the amount adsorbed and with temperature. For example, if the mobility characteristic of a polar substance in the liquid state were lost in the adsorbed state, the dielectric constant of the adsorbate would show no temperature coefficient. Measurement of the dielectric constant at different frequencies, moreover, might be expected to establish the 'relaxation time' (5) of the adsorbed molecules.

Previous work of this nature is limited. Argue and Maass (1) examined the system water–cellulose at one temperature and at a fixed frequency of 500 kc. Higuti (8) examined the system *n*-propyl alcohol – titanium dioxide gel over an extended temperature and frequency range. The heterodyne beat method was used in both these investigations. The present work differs from Higuti's in the technique employed, and in its restriction to a much smaller relative pressure range. The form of the curves over this limited range is studied in greater detail and with somewhat higher precision. It is believed that phenomena are revealed here which either did not occur, or were not detected, in the other investigation. Likewise, still other phenomena, abundantly clear from Higuti's work, do not occur under the conditions of this study.

Our preliminary investigations have been carried out using silica gel and several adsorbates. The results were obtained by two laboratory groups working in co-operation, at McGill University and at the National Research Council Laboratories, Ottawa. No extended discussion of the theoretical significance of the results will be attempted until the techniques of measurement and interpretation have been subjected to further test.

Experimental

The measurements consisted of the determination of the amount of vapor adsorbed by the silica gel in the condenser, and the simultaneous measurement of the capacity change resulting from the increment of adsorbate. A small correction was applied for the increase of capacity due to the free vapor in the cell. The reversibility of both the adsorption and capacity changes was established by measurement of the capacity decrements on desorption.

The capacity changes were measured by a bridge method, in the one laboratory at a fixed frequency of 3530 c.p.s., and in the other, at several frequencies ranging from 1000 to 60,000 c.p.s. The bridge was adapted for the purpose from a type described by Hartshorn (7). The increase in the capacity of the test condenser was compensated by a decrease in a variable condenser in parallel with it. The 'magnifying' arrangement of condensers described by Hartshorn was used, so that capacity changes of 0.01 $\mu\mu$f. or less could be read on the dial of a precision condenser. The reproducibility of a capacity change varied from ± 0.01 $\mu\mu$f. at the optimum frequencies (about 10,000 c.p.s.) to ± 0.2 $\mu\mu$f. at the least favorable frequency (60,000 c.p.s.). Since the changes of capacity for each addition of vapor ranged from 1 $\mu\mu$f. for butane to 5 or 6 $\mu\mu$f. for ethyl chloride and ethylene oxide, the accuracy of the measurements is in the neighborhood of 1 or 2%. This can be improved if the determinations are made at a fixed frequency in the optimum sensitivity range.

Presence of the adsorbate caused only negligible changes in the power factor of the test condenser except in the upper adsorption regions in the case of ethyl chloride. Consequently, if higher frequencies were to be investigated, the heterodyne beat method could be employed.

The dielectric cell finally adopted consisted of three concentric metal cylinders, retained in fixed relative positions by Pyrex glass spacers. In operation the inner and outermost electrodes were kept at ground potential.

The silica gel was a product of the Davison Chemical Corporation. The sieve sizes used in the two laboratories were 40 to 60 mesh and 45 to 80 mesh. The gel was evacuated *in situ* at a temperature of 120° C. under a pressure of 10^{-6} mm. of mercury.

The vapors used were ethyl chloride, *n*-butane, and ethylene oxide, obtained from the Ohio Chemical and Manufacturing Co. The materials were purified by distillation under vacuum from a dry ice – acetone trap to a liquid air trap, the middle fraction being retained.

A standard type of adsorption apparatus, similar to that described by Emmett (6, p. 3 *et seq.*) was used.

Results

When the change in capacity, $\triangle C$, is plotted against the amount adsorbed per gram of adsorbent, V, a plot is obtained that appears to consist of two or more quite distinct sections. Each of these sections approximates to linearity. The slight 'scattering' of experimental points is almost random relative to a straight median line, although a slight tendency toward curvature is noted in some experiments. Two curves for each substance, typical of a larger number of runs, are given in Figs. 1, 2, and 3. The points of discontinuity are approximately located on these plots. In Table I are presented typical values of the ratio of capacity increase to volume increase, $\triangle C/\triangle V$, obtained in successive additions of adsorbate. The results are given only to two significant figures, since the accuracy of the measurements scarcely justifies the retention of the third figure. This procedure has the advantage of directing attention to the reality of the discontinuities in slope, the feature of greatest importance.

In all cases studied, the discontinuous change of dielectric constant of the adsorbate corresponding to the change in slope of the ΔC vs. V curve indicates a decrease in this quantity. In other words, the portion of the adsorbate

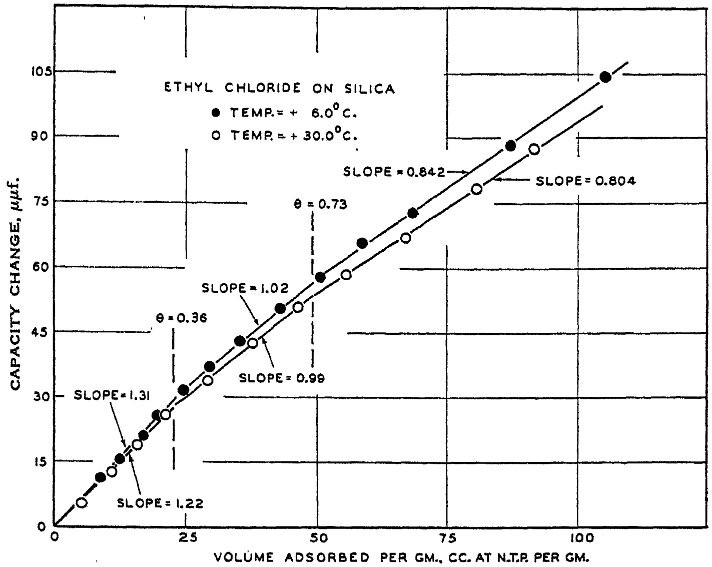

FIG. 1. *Effect of adsorbed ethyl chloride on the capacity of a condenser containing silica gel.*

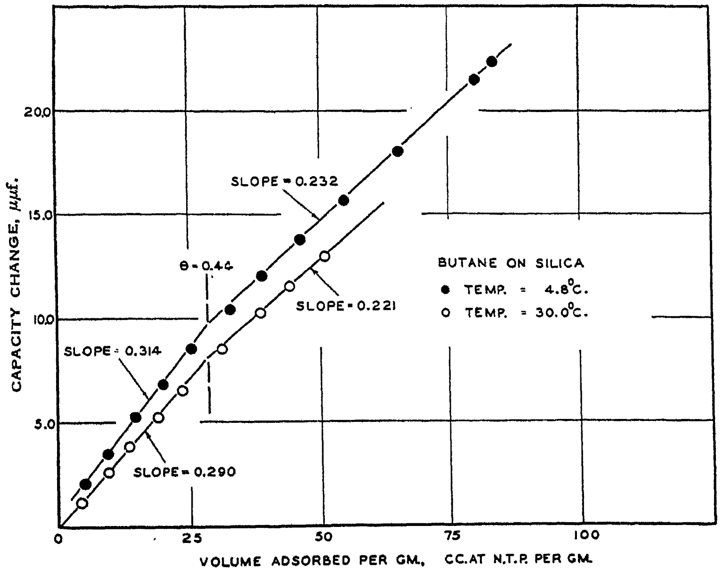

FIG. 2. *Effect of adsorbed butane on the capacity of a condenser containing silica gel.*

corresponding to the second 'linear' region has a lower dielectric constant than the portion corresponding to the first region. Three such regions were found for ethyl chloride (Fig. 1). In terms of the amount adsorbed, the two breaks in the ΔC vs. V plots occur at about 23 and 48 cc. of vapor (N.T.P.) per gram of silica gel. Although it is difficult to locate the break points with high precision, it appears that their positions, expressed in terms of amount adsorbed, do not vary with temperature.

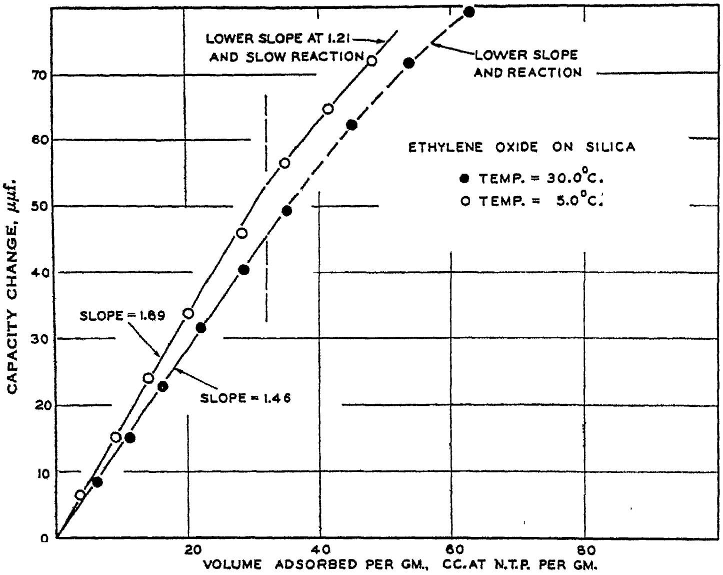

FIG. 3. *Effect of adsorbed ethylene oxide on the capacity of a condenser containing silica gel.*

The temperature coefficients of the slopes ΔC vs. V are very small. Thus, for an increase of temperature from 6° to 30° C., the slopes of the three sections each decreased about 3 to 6%. Since this temperature coefficient is much smaller than that which would be expected for liquid ethyl chloride, it was decided to investigate the temperature coefficient for the dielectric constant of *n*-butane, a typical non-polar substance, under the same conditions. The apparent temperature coefficient of the adsorbed butane proved to be the same, within the limits of experimental error, as that of the adsorbed ethyl chloride. This suggests either that the ethyl chloride dipoles are not free to rotate in the field, or that some effect, itself possessed of a temperature coefficient, is operating in such a way as to obscure the normal temperature dependence of dielectric constant for ethyl chloride. One such possibility is that of association between the adsorbed molecules of ethyl chloride.

From a study of the dielectric constant of the adsorbate over sufficiently wide ranges of temperature and frequency, it might be possible to choose between two such alternatives, particularly if anomalous dispersion were

TABLE I

Adsorption increment, cc. at N.T.P.	Total volume, cc. at N.T.P.	$\frac{\text{Capacity increment}}{\text{Volume increment}}; \frac{\mu\mu\text{f.}}{\text{cc. at N.T.P.}}$	
Ethyl chloride at 6.0° C.—Frequency, 10,000 c.p.s.			
50.9	50.9	0.23	Section I
19.2	70.1	0.22	
26.5	96.6	0.22	
18.5	115.1	0.22	
27.6	142.7	0.21	
29.2	171.9	0.20	Intermediate
34.9	206.8	0.17	Section II
43.3	250.1	0.17	
44.2	294.3	0.16	
45.2	340	0.15	Section III
56.5	396	0.15	
109.1	505	0.15	
110.2	615	0.15	
Ethylene oxide at 30° C.—Frequency, 10,000 c.p.s.			
33.9	33.9	0.25	Section I
28.9	62.8	0.24	
31.8	94.6	0.25	
33.8	128.4	0.25	
36.4	164.8	0.25	
40.9	205.7	0.21	Section II
57.3	263.0	0.22	
		(Reaction causing appreciable drift)	
Butane at 30.0° C.—Frequency, 10,000 c.p.s.			
23.6	23.6	0.050	Section I
28.1	61.7	0.052	
25.3	87.0	0.050	
27.9	114.9	0.048	
30.5	145.4	0.042	Section II
45.6	191.0	0.042	
41.8	232.8	0.042	

found to occur. As Table II, showing the dependence of capacity change on frequency, indicates, no anomalous dispersion was found in the frequency range studied, for any of the three adsorbates.

On the assumption of the validity of certain adsorption theories, some inferences can be made respecting the molecularity of the adsorbed layer, the fraction of the surface covered, and so on. It might be expected that some

TABLE II

EXAMPLES OF THE INDEPENDENCE OF MEASURED CAPACITY CHANGE AND FREQUENCY

Compound	Frequency	Measured capacity change	Temperature, ° C.
Ethyl chloride	1,000	5.83 ± 0.04	30.0
	10,000	5.82 ± 0.01	
	20,000	5.81 ± 0.03	
	40,000	5.74 ± 0.1	
	60,000	6.00 ± 0.2	
Butane	1,000	1.42 ± 0.04	4.8
	10,000	1.42 ± 0.01	
	20,000	1.41 ± 0.03	
	40,000	1.40 ± 0.1	
	60,000	1.40 ± 0.2	
Ethylene oxide	1,000	8.48 ± 0.04	30.0
	10,000	8.42 ± 0.01	
	20,000	8.42 ± 0.03	
	40,000	8.45 ± 0.1	
	60,000	8.34 ± 0.2	

relation between such inferred properties and the form of the ΔC vs. V curve would be evident. For example, it is possible to calculate the fraction, θ, of the surface covered by adsorbate, utilizing the Brunauer–Emmett–Teller theory as extended by T. L. Hill (9). Thus, if the change in the dielectric constant of the adsorbate were due to regions of differing nature on the adsorbent surface, it might be thought that the breaks in the ΔC vs. V curves should occur at approximately the same values of θ for different substances. In Table III are given the values of the quantities V_m, C, and θ deduced from

TABLE III

SUMMARY OF ADSORPTION DATA—B.E.T. VALUES

Compound	Temperature, ° C.	Relative pressure range investigated	V_m, cc. at N.T.P./gm.	C	Fraction of surface covered (θ) at breaks
Butane	4.8	0.0–0.4	54.0 Multilayer formula	7.7	0.44
	30.0	0.0–0.3	54.4	6.3	0.44
Ethyl chloride	6.0	0.0–0.6	62.2 Multilayer formula	27.7	0.36, 0.73
	30.0	0.0–0.5	60.7	25.7	0.36, 0.73
Ethylene oxide*	5.0	0.0–0.03	—	—	—
	30.0	0.0–0.09	55.2 Monolayer	348	—

* *The adsorption data for ethylene oxide are not well represented by either the monolayer or multilayer formula.*

the Brunauer–Emmett–Teller adsorption equation. The first two quantities are defined as follows:

V_m = the volume of vapor (N.T.P.) required to form a monolayer,

C = a quantity related exponentially to the difference in heat of evaporation between the first layer and succeeding layers of adsorbate.

It is evident that no simple correlation exists.

No trend of the dielectric constant of the adsorbate toward that of the bulk liquid is observed in the range studied as the degree of saturation or number of adsorbed layers increases. This is in contrast to the results of Higuti (8) who, however, worked over a more extended relative pressure range. These conclusions are based on a comparison of the calculated values for the dielectric constant of the adsorbate with those calculated for the bulk liquids. The latter were calculated from available data for permanent moments, densities and refractivities using the Onsager equation (11). Where possible the values so computed were compared with dielectric constant data in the literature.

Preliminary calculations tend to justify the use of Equation (2). Butane, having no permanent moment, is more likely to have the same value for the dielectric constant in the adsorbed and bulk liquid phases. The values calculated for the adsorbed film (assuming normal liquid density) at 30° C. are 1.84 for the first, and 1.57 for the second section of the ΔC vs. V plot. The value calculated for the bulk liquid at 30° C. is 1.77. Extending this procedure to ethyl chloride, typical data for the first, second, and third sections give values for the dielectric constant of the adsorbate of 5.75, 4.84, and 4.12, respectively at 30° C. These may be compared with the value of 9.4 calculated for liquid ethyl chloride at the same temperature.

In the study of ethylene oxide it was found that the values of capacity drifted with time toward lower values once an amount of about 40 cc. per gm. of gas had been adsorbed. This finding suggests that polymerization of the adsorbate was occurring. From the variation in the rate of drift with temperature, the value of the Arrhenius activation energy was calculated to be 8 kcal. per mole.

Below the apparently critical degree of surface saturation the capacity values were constant, and it is apparent that the temperature coefficient of the dielectric constant for adsorbed ethylene oxide is about 15% for the temperature interval, a value almost identical with that for the computed dielectric constant for the bulk liquid.

A correlation between the slopes of the straight line regions of the ΔC vs. V plots and the calculated liquid dielectric constants was attempted. If the slope of these regions is directly related to the dielectric constant of the bulk liquid, then the ratio of slope to dielectric constant should be independent of temperature and have the same value for the various substances. It is seen from Table IV that these criteria are not met.

TABLE IV

Compound	Dielectric constant of liquid by Onsager formula	Slope of linear sections			Slope of linear sections divided by dielectric constant			Temperature, ° C.
		Section 1	Section 2	Section 3	Section 1	Section 2	Section 3	
Ethyl chloride	9.4	1.22	0.990	0.804	0.130	0.105	0.0856	30.0
Butane	1.77	0.314	0.232	—	0.177	0.131	—	30.0
Ethylene oxide	11.2	1.46	—	—	0.130	—	—	30.0
Ethyl chloride	10.7	1.31	1.02	0.842	0.122	0.0953	0.0786	6.0
Butane	1.81	0.290	0.221	—	0.160	0.122	—	4.8
Ethylene oxide	13.1	1.69	1.21	—	0.129	0.0924	—	5.0

Conclusion

Further experimental data are required before these results can be satisfactorily interpreted. In the meantime, however, our tentative conclusions may be summarized as follows:

(1). The dielectric constants of adsorbed butane and ethyl chloride show the same very small temperature coefficient. Adsorbed ethyl chloride thus behaves like a non-polar compound, owing possibly to restricted mobility, or to a temperature dependent molecular association.

(2). In all cases studied, it appears that the adsorbate consists of two or more portions having different dielectric constants. This is perhaps due to differences in the nature of the adsorption.

(3). The calculated dielectric constant of adsorbed ethyl chloride is significantly lower than that calculated for the bulk liquid. In the absence of direct experimental data for the latter, this discrepancy might also be attributed to restricted mobility or to molecular association.

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APPLICATION DE LA RÉACTION DE MEERWEIN À LA SYNTHÈSE DE DÉRIVÉS DU STILBÈNE ET DU DISTYRYLE[2]

PAR PHILIBERT L'ECUYER[2] ET FRANÇOIS TURCOTTE[3]

Résumé

Par la réaction de Meerwein entre l'acide cinnamique et des sels de diazonium convenablement substitués, les *o*-, *m*- et *p*-distyrylbenzènes ont été préparés. La même réaction entre l'acide *m*-nitrocinnamique et les trois nitranilines a donné naissance aux trois dinitrostilbènes correspondants. D'autre part l'acide cinnaménylacrylique et les sels diazoniums appropriés ont conduit au *m*-nitrodiphénylbutadiène, à l'*o*- et au *p*-méthoxydiphénylbutadiène, ainsi qu'aux *m*- et *p*-styryldiphénylbutadiènes. Le *p*-méthoxydiphénylbutadiène, par réaction de Diels et Alder, a formé un composé d'addition.

Introduction

La réaction de Meerwein (15) entre les sels de diazonium aromatiques et les composés carbonyles possédant une double liaison entre les carbones α et β, présente, lorsqu'appliquée aux acides cinnamiques, un moyen d'accès nouveau à certains dérivés du stilbène (I, R:H) et du distyryle (II, R:H).

Le sel de diazonium préparé, suivant les méthodes ordinaires, en milieu chlorhydrique aqueux, est versé dans une solution du composé carbonyle dans l'acétone, en présence d'acétate de sodium comme tampon et de chlorure cuivrique comme catalyseur. La réaction est accompagnée d'un dégagement gazeux et d'une élévation considérable de température. Il y a avantage à maintenir le mélange réactionnel à la plus basse température qui permette le dégagement gazeux, alors que la réaction de Meerwein domine les réactions secondaires possibles:

a) réaction de type Sandmeyer,

b) déamination par l'acétone (16),

c) formation de résines de nature encore obscure (15),

qui se passent à des températures plus élevées, pour un sel de diazonium donné.

On isole le produit de la réaction par la distillation à la vapeur d'eau et la décantation de la liqueur résiduelle. On extrait ensuite le résidu au benzène, s'il ne se solidifie pas par refroidissement. En tous cas, on lave la solution benzénique ou le résidu à l'ammoniaque et on soumet le produit sec à la distillation sous une pression variant de 0.01 à 0.001 mm. de mercure. La substance ainsi obtenue contient le groupement aryle fixé au carbone α du composé carbonyle de départ.

Depuis sa découverte, en 1939, cette méthode de synthèse fut appliquée avec succès aux acides carbalkoxy-cinnamiques par Fuson et Cooke (11),

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[1] *Manuscrit reçu le 28 avril 1947.*
Contribution du Département de Chimie de l'Université Laval, Québec, Qué.

[2] *Professeur de Chimie organiqne.*

[3] *Etudiant à l'Ecole des Gradués et boursier de la Canadian Industries Limited.*

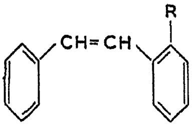
ainsi qu'aux amines halogénées ou alkylées par Bergmann et ses collaborateurs (4, 5, 6). Ces derniers introduisirent en outre l'usage de l'acide cinnaménylacrylique, le vinylogue de l'acide cinnamique. Bergmann a également obtenu des résultats favorables avec les sels de diazonium dérivés des naphtylamines et du *p*-aminodiphényle (5, 6).

Le but du présent travail fut d'abord la préparation des trois distyrylbenzènes (I, III, V, $R : CH = CH-C_6H_5$), en appliquant la méthode de Meerwein aux sels de diazonium des *o*-, *m*- et *p*-aminostilbènes en conjonction avec l'acide cinnamique. Le *p*-distyrylbenzène avait déjà été préparé par Kauffmann (13), qui condensa, à cet effet, le chlorure de benzylmagnésium avec l'aldéhyde téréphtalique, selon la méthode de Grignard, et déshydrata par pyrolyse le dérivé acétylé du dialcool obtenu. Récemment Blout et Eager (8) rapportaient, par une méthode identique comportant l'usage de l'aldéhyde isophtalique, la synthèse du *m*-distyrylbenzène.

La condensation des trois aminostilbènes avec l'acide cinnamique s'effectue avantageusement à des températures inférieures à 20° C. et, comme Bergmann l'a déjà signalé dans le cas des chloranilines, avec des rendements variant, suivant la position de substituant styryle sur le noyau aromatique du sel de diazonium, dans l'ordre ortho < méta < para. Les résultats que nous avons obtenus pour le *m*-nitrostilbène le situent à cet égard entre l'*o*- et le *p*-nitrostilbène, ce qui confirme une fois de plus cette gradation dans les rendements. Des trois distyrylbenzènes, l'ortho et le para (I, V, $R : CH = CH-C_6H_5$) dont les doubles liaisons sont conjuguées d'une extrémité à l'autre de la molécule, sont jaunes, tandis que le méta (III, $R : CH = CH-C_6H_5$) dans lequel la conjugaison des doubles liaisons s'arrête au noyau central, est incolore. C'est d'ailleurs ce à quoi on devait s'attendre.

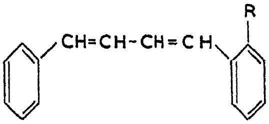
La seconde partie de ce travail avait pour objet d'étudier l'utilisation des acides cinnamiques substitués à la synthèse de stilbènes avec des groupements substituants dans les deux anneaux benzéniques. La réaction de Bischoff (7) entre les chlorures de nitrobenzyle et la potasse alcoolique ne donne que des dérivés symétriquement substitués; tandis que la réaction de Perkin ne convient pas à tous les cas. Il est maintenant évident qu'en employant, dans la réaction de Meerwein, des produits de départ convenablement substitués, on pourra préparer tous les composés prévus par la théorie, symétriques ou non.

A cet effet, nous avons employé comme composé carbonyle α, β nonsaturé l'acide *m*-nitrocinnamique qui, avec les sels de diazonium obtenus des *o*-, *m*- et *p*-nitranilines, a donné naissance au 3,2'-dinitrostilbène (VII), au 3,3'-dinitrostilbène (VIII) et au 3,4'-dinitrostilbène (IX). Cullinane (10) prétend avoir préparé ce dernier en effectuant la réaction de Perkin entre l'acide *p*-nitrophénylacétique et la *m*-nitrobenzaldéhyde. Il l'aurait obtenu de l'acide acétique sous forme de cristaux jaunes de p.f. 155° C. qui exhibent une fluorescence verte en solution dans l'éthanol ou l'acétone. Cependant Harrison et Wood (12) furent incapables de reproduire les résultats de



R: H, OMe, NO_2 ou $CH=CH-C_6H_5$

I



R: H ou OMe

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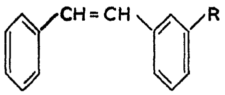
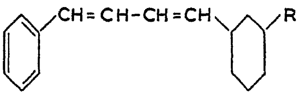


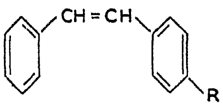
R: NO_2, NH_2 ou $CH=CH-C_6H_5$

III



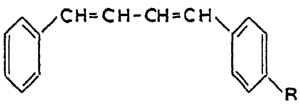
R: NO_2 ou $CH=CH-C_6H_5$

IV



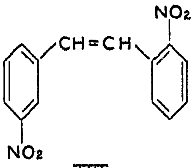
R: NO_2 ou $CH=CH-C_6H_5$

V



R: OMe ou $CH=CH-C_6H_5$

VI



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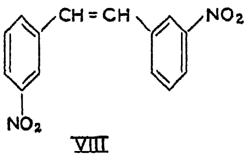
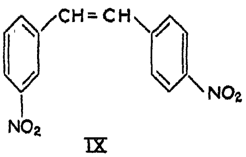


VIII



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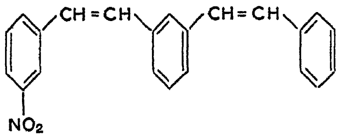
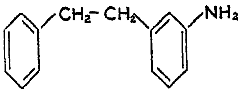
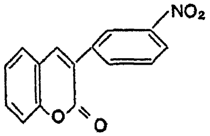


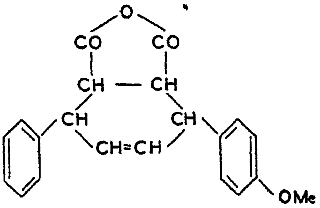
X



XI



XII



XIII

Cullinane, et obtinrent, en opérant dans les mêmes conditions, le dinitrostilbène (IX) fondant à 217° C., dont les solutions ne manifestent aucune fluorescence. Les propriétés physiques du composé obtenu par la réaction de Meerwein semblent donner raison à ces derniers.

Pour la préparation des dérivés du 1,4-diphénylbutadiène (II, R:H) ou distyryle, la méthode est sensiblement la même que pour celle des dérivés du stilbène. Le composé carbonyle est ici l'acide cinnaménylacrylique ou cinnamalacétique. L'emploi d'une plus grande quantité d'acétone est alors nécessaire pour assurer la complète solubilité de l'acide au moment de l'introduction de la solution aqueuse du sel de diazonium. La température de dégagement d'azote est généralement un peu plus élevée et les rendements se comparent assez bien à ceux que l'on obtient avec l'acide cinnamique. Le radical aryle se fixe au carbone α et l'élimination de l'anhydride carbonique est aussi spontanée.

La condensation des sels de diazonium des *m*- et *p*-aminostilbènes a permis la synthèse du 1-(*m*-styrylphényl)-4-phénylbutadiène-1,3 (IV, R : $CH = CH-C_6H_5$) et du 1-(*p*-styrylphényl)-4-phénylbutadiène-1,3 (VI, R : $CH = CH-C_6H_5$) respectivement.

Au début de la sublimation de ces deux derniers composés dans un vide de 0.001 mm. de mercure nous avons isolé du stilbène. Nous y voyons l'indice de l'importance relative d'une réaction secondaire prévue, mais non confirmée dans les synthèses précédentes, à savoir l'action réductrice de l'acétone sur les sels de diazonium. En effet, contrairement au stilbène, le nitrobenzène et l'anisole, les produits qui dans les condensations antérieures auraient pu se former grâce à cette réaction secondaire, sont volatils à la vapeur d'eau et sont éliminés durant cette opération. Néanmoins le rendement est satisfaisant dans les deux cas. Encore ici, le composé (VI, R:$CH = CH-C_6H_5$) complètement conjugué est jaune contrairement à l'autre (IV, R:$CH = CH-C_6H_5$) qui est incolore.

Deux autres dérivés du distyryle, portant un groupement méthoxyle substitué sur l'un des noyaux, furent préparés par la réaction de Meerwein, en faisant usage de l'*o*- et de la *p*-anisidine successivement, et de l'acide cinnamalacétique: ce sont le 1-(*o*-méthoxyphényl)-4-phénylbutadiène-1,3 (II, R:OMe) et le 1-(*p*-méthoxyphényl)-4-phénylbutadiène-1,3 (VI, R:OMe). Asano et Kameda (1) rapportent la synthèse de ce dernier. Ils l'ont isolé de la fraction insoluble dans la potasse du produit de la réaction de Perkin entre l'aldéhyde *p*-méthoxycinnamique et l'acide phénylacétique.

Enfin, il nous fut loisible de préparer, en solution dans le xylène, suivant la technique de Clar (9), un composé d'addition entre l'anhydride maléique et le composé (VI, R:OMe). Cette réaction se fait avec une extrême simplicité, le produit cristallisant du mélange réactionnel par refroidissement.

Les quelques synthèses que nous venons de citer, ajoutées à d'autres publications relativement peu nombreuses encore (2, 3, 4, 5, 6), permettent d'entrevoir les grandes possibilités de cette condensation de Meerwein entre les sels de diazonium et les composés carbonyles α, β non-saturés. Les rendements relativement faibles et les difficultés techniques de purification sont, dans plusieurs cas, compensés par l'accès facile des produits de départ et la généralité de l'application de la réaction.

Partie expérimentale

m-Nitrostilbène (III, R : NO_2)

Il a été préparé selon Bergmann (3), mais au lieu de triturer le produit de la réaction, celui-ci est distillé dans le vide. Le *m*-nitrostilbène distille à 160-170° C. (0.05 mm.) sous forme d'un solide jaune. Il cristallise de l'éthanol ou de l'acide acétique en longues aiguilles plates jaune serin de p.f. 112° C. Calculé pour $C_{14}H_{11}O_2N$: C,74.7; H,4.9%. Trouvé: C, 74.8; H, 5.3%.

3,3′-Dinitrostilbène (VIII)

Le chlorure de *m*-nitrobenzènediazonium est d'abord préparé par la diazotation de la *m*-nitraniline (13.8 g.; 0.1 mole) dans l'acide chlorhydrique à 25% (50 ml.) et la glace (50 g.) à l'aide d'une solution de nitrite de sodium (8.4 g.) dans l'eau (20 ml.). La solution du sel de diazonium est alors versée dans une solution froide (0° C.) d'acide *m*-nitrocinnamique (19.3 g.; 0.1 mole) dans l'acétone (600 ml.) contenant de l'acétate de sodium anhydre (20 g.) et du chlorure cuivrique hydraté (4 g.) en suspension. Un dégagement gazeux immédiat se produit à une température maintenue intentionnellement au-dessous de 0° C. et persiste pendant une heure et demie sous une vigoureuse agitation mécanique. La réaction est ensuite complétée en laissant le mélange prendre la température ambiante. Le mélange réactionnel est alors soumis à la distillation à la vapeur d'eau. Après la décantation du liquide chaud surnageant, le résidu brun gommeux se solidifie à froid. Il est pulvérisé, lavé plusieurs fois à l'ammoniaque 2 *N*, puis à l'eau et séché. Le 3,3′-dinitrostilbène se sublime à 175° C. (0.001 mm.). Il est insoluble dans l'éthanol et l'acétone, mais soluble dans le chloroforme et l'acide acétique bouillant. Il cristallise de ce dernier solvant en aiguilles jaune serin de p.f. 240-242° C. Le rendement du produit pur est de 5 g. (18%). Calculé pour $C_{14}H_{10}O_4N_2$: N, 10.3%. Trouvé: N, 9.9%.

3,2′-Dinitrostilbène (VII)

La réaction de Meerwein est effectuée comme précédemment à partir de 0.1 mole d'*o*-nitraniline et de 0.1 mole d'acide *m*-nitrocinnamique. Favorisé par une agitation mécanique énergique, le dégagement gazeux commence vers 8° C. et persiste pendant une heure et demie. Le 3,2′-dinitrostilbène se sublime à 160° C. (0.001 mm.). Il cristallise de l'alcool éthylique en aiguilles jaune orange de p.f. 150° C. Le rendement du produit pur est de 3.5 g. (12%). Calculé pour $C_{14}H_{10}O_4N_2$: N, 10.3%. Trouvé: N, 10.0%.

3,4′-Dinitrostilbène (IX)

La réaction de Meerwein est exécutée de la même façon à partir de la *p*-nitraniline (0.1 mole) et de l'acide *m*-nitrocinnamique (0.1 mole). Le dégagement gazeux se produit vers 12° C. et persiste pendant une heure. Du résidu sec de la réaction le 3,4-dinitrostilbène se sublime à 170° C. (0.001 mm.). C'est un solide insoluble dans l'éthanol qui cristallise de l'acide acétique en aiguilles jaune citron de p.f. 220-222° C. Le rendement du produit pur est de 7 g. (25%). Calculé pour $C_{14}H_{10}O_4N_2$: N, 10.3%. Trouvé: N, 10.2%.

o-Distyrylbenzène (*I*, $R : CH = CH-C_6H_5$)

L'*o*-aminostilbène (14 g.; 0.07 mole) dans l'acide chlorhydrique à 25% (30 ml.) et la glace (30 g.) est diazoté par l'addition d'une solution de nitrite de sodium (5.2 g.) dans l'eau (10 ml.). La solution du sel de diazonium est versée dans un mélange refroidi (0° C.) d'acide cinnamique (10.6 g.; 0.07 mole), d'acétone (100 ml.), d'acétate anhydre de sodium et de chlorure cuivrique hydraté (3.2 g.). Le dégagement gazeux se passe à 20° C. et dure une heure et demie. L'*o*-distyrylbenzène est isolé de la même façon que dans le cas du *m*-nitrostilbène. Il se sublime à 130-140°C. (0.001 mm.). Il cristallise de l'alcool éthylique en aiguilles jaunes de p.f. 120-122° C. Rendement du produit pur: 3 g. (15%).

m-Distyrylbenzène (*III*, $R : CH = CH-C_6H_5$)

La diazotation du *m*-aminostilbène et la réaction avec l'acide cinnamique sont réalisées exactement comme dans le cas précédent. Le dégagement gazeux se produit vers 12° C. et dure trois heures. Le *m*-distyrylbenzène se sublime entre 170-180° C. (0.001 mm.). Il est soluble dans l'éthanol et l'isopropanol à chaud, dans le benzène, le toluène et le chloroforme à froid. De l'acide acétique il cristallise en lamelles blanches de p.f. 182° C. Rendement du produit pur: 4 g. (20%). Calculé pour $C_{22}H_{18}$: C, 93.6; H, 6.4%. Trouvé: C, 93.3; H, 6.5%.

p-Distyrylbenzène (*V*, $R : CH = CH-C_6H_5$)

La réaction de Meerwein entre le *p*-aminostilbène et l'acide cinnamique est effectuée avec les mêmes quantités de substance et de la même façon que pour les autres distyrylbenzènes. Le dégagement gazeux se fait vers 25° C. et est terminé après deux heures d'agitation. Le *p*-distyrylbenzène se sublime à 150-160° C. (0.0005 mm.). C'est un solide insoluble dans la plupart des solvants organiques, mais soluble dans le chloroforme et le xylène. Il cristallise de ce dernier en aiguilles jaunes de p.f. 266° C. Le rendement du produit pur est de 7 g. (35%). Calculé pour $C_{22}H_{18}$: C, 93.6; H, 6.4%. Trouvé: C, 93.2; H, 6.5%.

3-(m-Nitrophényl)-coumarine (*XII*)

La solution du sel de diazonium préparé à partir de la *m*-nitraniline (34.5 g.; 0.25 mole) est versée dans une solution à 0° C. de coumarine (37 g.; 0.25 mole) dans l'acétone (200 ml.) contenant en suspension de l'acétate anhydre de sodium (50 g.) et du chlorure cuivrique hydraté (5 g.). Le dégagement gazeux se produit au-dessous de 20° C. et est terminé en moins d'une heure d'agitation. Le mélange réactionnel est traité comme auparavant et le résidu est trituré avec de l'éther (100 ml.), filtré, cristallisé trois fois de la pyridine, puis de l'acide acétique. La 3-(*m*-nitrophényl)-coumarine se sépare sous forme de cristaux blancs de p.f. 260-261° C. Calculé pour $C_{15}H_9O_4N$: N, 5.3%. Trouvé: N, 5.4%.

1-(m-Nitrophényl)-4-phénylbutadiène-1,3 (IV, R : CH = CH—C_6H_5)

Il a été préparé selon la méthode de Bergmann (3). Le solide brun obtenu en suivant la méthode d'isolation employée pour le 3,3'-dinitrostilbène est soumis à la sublimation dans le vide. Le 1-(*m*-nitrophényl)-4-phénylbutadiène-1,3 se dépose entre 160-180° C. (0.005 mm.). C'est un solide jaune qui cristallise de l'acide acétique. P.f. 145° C. Rendement de la substance pure: 3 g. (12%). Calculé pour $C_{16}H_{13}O_2N$: C, 76.5; H, 5.2%. Trouvé: C, 76.3; H, 5.5%.

1-(o-Méthoxyphényl)-4-phénylbutadiène-1,3 (II, R:OMe)

Le chlorure d'*o*-méthoxybenzènediazonium est préparé par la diazotation de l'*o*-anisidine (24.8 g.; 0.2 mole) dans l'acide chlorhydrique à 25% (50 ml.) et la glace (50 g.). Sa solution est ensuite versée dans un mélange froid (0° C.) d'acide cinnamalacétique (33.2 g.; 0.2 mole), d'acétate de sodium anhydre (40 g.), de chlorure cuivrique hydraté (8 g.) et d'acétone (600 ml.). Le dégagement gazeux se produit entre 10 et 15° C. et se continue pendant une heure. Le résidu de la réaction isolé de la façon ordinaire est distillé dans le vide. Le 1-(*o*-méthoxyphényl)-4-phénylbutadiène-1,3 distille entre 120-130° C. (0.01 mm.) sous la forme d'une huile qui, additionnée d'un peu d'éthanol dilué, se solidifie par refroidissement dans un mélange de glace sèche et d'acétone. Après cinq cristallisations de l'alcool éthylique dilué il apparaît sous forme d'aiguilles blanches de p.f. 74° C. Rendement: 7 g. (18%). Calculé pour $C_{17}H_{16}O$: C, 86.4; H, 6.8%. Trouvé: C, 86.1; H, 6.9%.

1-(p-Méthoxyphényl)-4-phénylbutadiène-1,3 (VI, R : OMe)

La réaction de Meerwein est exécutée à partir des mêmes quantités de *p*-anisidine et d'acide cinnamalacétique et de la même façon que dans le cas précédent. Le dégagement gazeux se passe entre 12 et 15° C. et est terminé après une heure d'agitation. Le 1-(*p*-méthoxyphényl)-4-phénylbutadiène-1,3 se sublime à 175° C. (0.01 mm.). Il est insoluble à froid dans l'alcool éthylique. De l'acide acétique il cristallise en aiguilles blanches de p.f. 162° C. Rendement du produit pur: 10 g. (22%). Calculé pour $C_{17}H_{16}O$: C, 86.4; H, 6.8%. Trouvé: C, 86.3; H, 6.9%.

Composé d'addition (XIII)

Un mélange de 1-(*p*-méthoxyphényl)-phénylbutadiène-1,3 (2 g.) et d'anhydride maléique (15 g.) dans le xylène (20 ml.) est maintenu à l'ébullition pendant environ 25 min. Il en résulte une solution claire dont le composé d'addition se sépare, par refroidissement, en aiguilles soyeuses blanches qui cristallisent de l'acide acétique. P.f. 193° C. Le rendement est quantitatif. Calculé pour $C_{21}H_{18}O_4$: C, 75.4; H, 5.4%. Trouvé: C, 75.1; H, 5.5%.

1-(p-Styrylphényl)-4-phénylbutadiène-1,3 (*VI, R* : $CH = CH-C_6H_5$)

La condensation de Meerwein est effectuée entre le sel de diazonium préparé à partir du *p*-aminostilbène (6 g.; 0.03 mole) et l'acide cinnamalacétique (5.5 g.; 0.03 mole). Le dégagement gazeux apparaît entre 20 et 25° C. et persiste pendant une heure et demie d'agitation mécanique continue. Le résidu de la réaction se sublime vers 175-180° C. (0.001 mm.). Le 1-(*p*-styrylphényl)-4-phénylbutadiène-1,3 cristallise de l'acide acétique en lamelles jaunes de p.f. 254-255° C. Rendement: 2.5 g. (25%). Calculé pour $C_{24}H_{20}$: C, 93.5; H, 6.5%. Trouvé: C, 93.2; H, 6.7%.

1-(m-Styrylphényl)-4-phénylbutadiène-1,3 (*IV, R* : $CH = CH-C_6H_5$)

Le *m*-aminostilbène (6 g.; 0.03 mole) dans l'acide chlorhydrique à 25% (20 ml.) additionné de glace (30 g.) est diazoté sous l'action d'une solution de nitrite de sodium (2 g.) dans l'eau (5 ml.). La liqueur diazotée est ensuite versée dans une suspension froide (0° C.) d'acétate de sodium anhydre (8 g.) et de chlorure cuivrique hydraté (1.5 g.) dans une solution d'acide cinnaménylacrylique (5.5 g.; 0.03 mole) dans l'acétone (150 ml.). Le mélange réactionnel est plongé dans un bain d'eau tiède et vers 20° C. il apparaît un dégagement gazeux qui dure pendant une heure et demie d'agitation mécanique. Le produit de la réaction est alors soumis au traitement habituel et le résidu est sublimé dans le vide. Le 1-(*m*-styrylphényl)-4-phénylbutadiène-1,3 se présente alors entre 150-160° C. (0.003 mm.). C'est un solide blanc insoluble à froid dans l'éthanol, soluble dans le benzène, le chloroforme et la pyridine. Il cristallise de l'acide acétique. P.f. 159° C. Calculé pour $C_{24}H_{20}$: C, 93.5; H, 6.5%. Trouvé: C, 93.3; H, 6.6%.

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The Preparation of 1,10-Phenanthroline From *o*-Phenylenediamine

The preparation of 1,10-phenanthroline from *o*-phenylenediamine was carried out by Blau (1), with a reported yield of 30%, but the experimental details were not recorded, and his work has not been duplicated. Hieber and Mühlbauer (2) reported an 18% yield by this synthesis. Smith and Richter (4, 6), and Smith (5) have reported this method of preparation of 1,10-phenanthroline to be unsuccessful, and they state that the desired reactions are accompanied by so many side reactions that the isolation of the pure base is very difficult. We have found that if the method of Hieber and Mühlbauer is followed closely, a yield of nearly 20% of the base may be obtained.

EXPERIMENTAL

o-Phenylenediamine (30 gm.), dry glycerol (165 gm.), and arsenic pentoxide (78.9 gm.) were mixed well, and concentrated sulphuric acid (sp. gr. 1.84, 150 gm.) was added. The resultant mixture was dark red and quite fluid. The mixture was heated, using an oil bath, until it began to reflux, after which the temperature of the reaction mixture was maintained just high enough to cause very gentle refluxing. The bath temperature was held to a maximum of 10° C. above the reaction mixture temperature. The mixture was refluxed for 15 hr., then diluted with three times its volume of warm water. The mixture was filtered and the filtrate was carefully neutralized to litmus with 10 *N* sodium hydroxide, then acidified with 4 ml. of 3 *N* sulphuric acid. The black tarry precipitate formed was filtered off and extracted with 330 ml. of hot 3 *N* sulphuric acid. To the extract plus the filtrate was added a solution of 90 gm. mercuric chloride in 700 ml. hot water. The fine brown precipitate that formed was allowed to settle and was filtered off. The filtrate was green.

The precipitate was decomposed by suspending it in 700 ml. hot water and saturating the hot mixture with hydrogen sulphide. The mercuric sulphide formed was filtered off, and the filtrate made alkaline with 40 ml. of 10 *N* sodium hydroxide, a black tarry suspension being formed. The mixture was evaporated on the water bath as far as possible, and the solid dried for one hour at 130° C. The dry residue was distilled under 3 mm. pressure, a yellow oil distilling over between 150° and 190° C. On recrystallizing the solidified product from water, 9.7 gm. of 1,10-phenanthroline monohydrate, m.p. 103° to 103.5° C., was obtained. This is a yield of 17.6%.

The above procedure was repeated four times by two different workers, in two cases with a reflux time of eight hours, and the yields obtained averaged 11 gm. (20%).

An attempt to modify the reaction using boric acid reduced the yield to 1%. Use of the acetylated amine, as suggested by Manske *et al.* (3), gave a 0.7% yield, while a reduction in the amount of sulphuric acid to 99 gm. lowered the yield to 2.7%. The critical feature of the reaction is apparently the temperature of refluxing; if this is allowed to rise even slightly for a short time, there is practically no yield. The time of reflux did not seem to affect the yield appreciably, and the eight hour period may be longer than necessary; Hieber and Mühlbauer (2) record two to three hours.

The green filtrate obtained when the mercury salt of 1,10-phenanthroline was filtered off contained an unidentified by-product, which behaved as an acid–base indicator, turning purple above pH 5.5 and green below pH 4.7.

We wish to acknowledge the assistance of Messrs. D. Aziz, E. C. Gain, and D. M. Steiner with the experimental work.

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DEPARTMENT OF CHEMICAL ENGINEERING,
UNIVERSITY OF TORONTO,
TORONTO, ONT.

J. G. BRECKENRIDGE
S. A. G. SINGER

SECTION B

INDEX TO VOLUME 25

Authors

Allenby, O. C. W. and Wright, G. F—Dimethyldinitroöxamide, 295.

Ascah, R. G.—See Janz, G. J.

Ashford, W. R., Evans, T. H., and Hibbert, H.—Studies on reactions relating to carbohydrates and polysaccharides. *LXIII. The stability of maltose and cellobiose octanitrates, 155.

———— and Hibbert, H.—Studies on reactions relating to carbohydrates and polysaccharides. *LXII. Effect of hot alkali on the nitrates of starch, amylose, and amylopectin, 151.

Baker, B. E.—See Leitch, L. C.

Bardwell, J. and Sivertz, C.—The determination of particle size by light scattering, 255.

Barnett, H. W., Davis, R. G., and Graham, R. P.—The preparation of cyanogen chloride, 289.

Bell, H. J. and Jaques, L. B.—An acetyl derivative of heparin, 472.

Blackwood, A. C., Neish, A. C., Brown, W. E., and Ledingham, G. A.—Production and properties of 2,3-butanediol. XVII. Fermentation of glucose by strains of *Bacillus subtilis*, 56.
See Neish, A. C.

Bond, W. J., Goddard, I. G., and Wright, G. F—The isolation of sassafras lignin, 535.

Boomer, E. H. and Naldrett, S. N.—The oxidation of methane at high pressures. IV. Experiments using pure methane and copper, silver, zinc, nickel, or Monel metal as catalysts, 494.

Boulet, M., Nelson, J. A., and McFarlane, W. D.—A rapid colorimetric method for the determination of lysine in protein hydrolysates, 540.

Bourns, A. N. and Nicholls, R. V. V.—The catalytic action of aluminium silicates. I. The dehydration of butanediol-2,3 and butanone-2 over activated Morden bentonite, 80.

Boyd, M. L. and Winkler, C. A.—Studies on the formation of hexamine, 387.
See Campbell, A. N.

Breckenridge, J. G. and Herbst, J. H. E.—Fractionation of the reaction product of linseed oil and glycerol, 420.

———— and Singer, S. A. G.—5-Hydroxyquinoline-8-carboxylic acid—a colorimetric reagent for ruthenium, 49. The preparation of 1,10-phenanthroline from *o*-phenylenediamine, 583.

Brickman, L.—See Leitch, L. C.

Brown, W. E.—See Blackwood, A. C.

Campbell, A. J. R.—See Campbell, A. N.

Campbell, A. N. and Campbell, A. J. R.—Binary and ternary eutectics involving ammonium nitrate, 90.

———— and Kushnarov, H. A.—A study of systems involving trinitrotoluene, RDX, NENO, and dinitrobenzene, with particular reference to the composition of the binary eutectics, 216.

———— and Lemaire, H. P.—The chromates of silver and copper, 243.

———— and Miller, S. I.—A method of analysis for the system: benzene - ethyl alcohol - carbon tetrachloride, 228.

* *See Errata at the end of the Subject Index.*

Campbell, A. N. and Pritchard, E. J.—The equilibrium diagrams and crystallization velocities of the systems: (a) picric acid – 2,4-dinitrophenol; (b) dinitrophenol – trinitrotoluene; (c) picric acid – dinitrophenol – trinitrotoluene, 183.
————, Pritchard, E. J., Campbell, A. J. R., and Boyd, M. L.—The equilibrium data and crystallization characteristics of the system: picric acid – dinitrophenol – picramide, 211.

Campbell, R. B.—See Young, E. G.

Carroll, K. K. and Wright, R. H.—Compound formation in the system urotropine – acetic acid.
I. The phase diagram, 477.
II. Raman spectrum measurements, 481.

Coffin, C. C. and Long, B. F.—The heterogeneity of activated cocoanut-shell charcoal, 502.

Cragg, L. H., Rogers, T. M., and Henderson, D. A.—The evaluation of the intrinsic viscosity (as intrinsic flow time) of GR-S in benzene, 333.
See Rogers, T. M.

DeLuca, H. A.—Photometric microdetermination of calcium, 449.

Davis, R. G.—See Barnett, H. W.

Douglas, D. E. and Winkler, C. A.—The preparation, purification, physical properties, and hydrolysis of cyanogen chloride, 381.

Eastwood, T. A., Garmaise, D. L., Morantz, D. J., and Winkler, C. A.—Studies in the formation of DDT, 509.

Evans, T. H.—See Ashford, W. R.

Farmilo, C. G.—See Marion, L.

Fineman, M. N. and Puddington, I. E.—Measurements of cure of some thermosetting resins, 101.

Gagnon, P. E., Savard, K., Gaudry, R., and Richardson, E. M.—Synthesis of amino acids from substituted cyanoacetic esters. 4-Alkyl-3-aminopyrazolones, 28.

Garmaise, D. L.—See Eastwood, T. A.

Gaudry, R.—See Gagnon, P. E.

Giguère, P. A.—The thermal decomposition of hydrogen peroxide vapor. II, 135.

Gillespie, T.—See Langstroth, G. O.

Goddard, I. G.—See Bond, W. J.

Graham, R. P.—See Barnett, H. W.

Graham, W., Hutcheon, A. T., and Spinks, J. W. T.—Catalytic aromatization of Turner Valley crudes, 108.

Grummitt, W. E., Guéron, J., Wilkinson, G., and Yaffe, L.—The growth of La^{140} (40 hours) from Ba^{140} (12.7 days), 357. The fission yields of Ba^{139} and Ba^{140} in neutron fission of U^{235} and U^{238}, 364.

Guéron, J.—See Grummitt, W. E.

Haskell, V. C.—See Neish, A. C.

Hawkes, A. S. and Winkler, C. A.—The thermal explosion of lead azide, 548.

Hawkings, R. C., Simpson, D., and Thode, H. G.—The polarographic determination of tin in high purity zinc and zinc die-casting alloys, 322.
See McGilvery, J.

Henderson, D. A.—See Cragg, L. H.; Rogers, T. M.

Herbst, J. H. E.—See Breckenridge, J. G.

Hibbert, H.—See Ashford, W. R.

Hollies, N.—See McIntosh, R.

Hutcheon, A. T.—See Graham, W.

Janz, G. J.—Concerning the theoretical aspects of the reaction of cyanogen and 1,3-butadiene, 331.
———, Ascah, R. G., and Keenan, A. G.—The reaction of cyanogen with 1,3-butadiene, 272.
——— and Keenan, A. G.—The preparation of 2-cyanopyridines from cyanogen and some simple 1,3-dienes, 283.

Jaques, L. B.—See Bell, H. J.

Johnson, H. S.—See McIntosh, R.

Keenan, A. G.—See Janz, G. J.

Kulka, M.—See Manske, R. H. F.

Kushnarov, H. A.—See Campbell, A. N.

Langstroth, G. O. and Gillespie, T.—Coagulation and surface losses in disperse systems in still and turbulent air, 455.

L'Ecuyer, P. and Turcotte, F.—Application de la réaction de Meerwein à la synthèse de dérivés du stilbene et du distyryle, 575.

Ledingham, G. A.—See Blackwood, A. C.; Neish, A. C.

Leitch, L. C., Baker, B. E., and Brickman, L.—Sulphanilamidopyrimidines, 14.

Lemaire, H. P.—See Campbell, A. N.

Lemieux, R. U. and Morrison, J. L.—The adsorption of aliphatic acids on activated charcoals, 440.
——— and Purves, C. B.—Quantitative estimation as acetic acid of acetyl, ethylidene, ethoxy, and α-hydroxyethyl groups, 485.

Long, B. F.—See Coffin, C. C.

Lossing, F. P., Shields, R. B., and Thode, H. G.—A recording unit and electronic shunt selector for a mass spectrometer, 397.

Macdonald, F. J.—See Neish, A. C.

Macdonald, W. C.—See Potter, C.

McFarlane, W. D.—See Boulet, M.

McGilvery J., Hawkings, R. C., and Thode, H. G.—A note on the use of multi-tip electrodes in polarographic work, 132.

McIntosh, R. L., Johnson, H. S., Hollies, N., and McLeod, L.—Preliminary observations of the dielectric constants of vapors adsorbed on activated silica, 566.
See Sirianni, A. F.

Mackintosh, C. E.—See Yaffe, L.

McLaughlin, R. R.—See Potter, C.

McLeod, L.—See McIntosh, R. L.

Manske, R. H. F. and Kulka, M.—The synthesis of some carbazole derivatives, 376.

Marion, L. and Farmilo, C. G.—Note on the preparation of 1-methoxy-1,3-butadiene, 118.
———— and Oldfield, C. W.—The synthesis and the characterization of monomethyl- and dimethylindoles, 1.

Miller, S. I.—See Campbell, A. N.

Mitton, H. E.—See Van Cleave, A. B.

Morantz, D. J.—See Eastwood, T. A.

Morrison, J. L.—See Lemieux, R. U.

Morton, M. and Nicholls, R. V. V.—Tertiary mercaptans as modifiers in GR-S polymerizations, 159.

Naldrett, S. N.—See Boomer, E. H.

Neish, A. C.—Production and properties of 2,3-butanediol. XXIII. Condensation of the isomeric 2,3-butanediols with ethyl acetoacetate, 423.
————, Blackwood, A. C., Robertson, F. M., and Ledingham, G. A.—Production and properties of 2,3-butanediol. XVIII. Dissimilation of glucose by *Serratia marcescens*, 65.
————, Haskell, V. C., and Macdonald, F. J.—Production and properties of 2,3-butanediol. XXI. Catalytic cracking of cyclic acetals and ketals derived from 2,3-butanediol, 266.
———— and Macdonald, F. J.—Production and properties of 2,3-butanediol. XIX. Cyclic acetals and ketals derived from *levo*-2,3-butanediol, 70.
See Blackwood, A. C.; Robertson, F. M.

Nelson, J. A.—See Boulet, M.

Nicholls, R. V. V.—See Bourns, A. N.; Morton, M.; Polley, J. R.

Oldfield, C. W.—See Marion, L.

Polley, J. R., Winkler, C. A., and Nicholls, R. V. V. Studies on the formation of hexamine from formaldehyde and ammonium salts in aqueous solution, 525.

Potter, C. and Macdonald, W. C.—The kinetics of consecutive second order reactions, 415.
———— and McLaughlin, R. R.—The kinetics of the formation of ethanolamines, 405.

Pritchard, E. J.—See Campbell, A. N.

Puddington, I. E.—See Fineman, M. N.; Southam, F. W.

Purves, C. B.—See Lemieux, R. U.

Richardson, E. M.—See Gagnon, P. E.

Robertson, F. M. and Neish, A. C.—Production and properties of 2,3-butanediol. XXIV. The cyclic sulphites of *meso*- and *levo*-2,3-butanediol, 491.
See Neish, A. C.

Rogers, T. M., Henderson, D. A., and Cragg, L. H.—A note on the variation with temperature of the intrinsic viscosity of GR-S in benzene, 351.
See Cragg, L. H.

Savard, K.—See Gagnon, P. E.

Shields, R. B.—See Lossing, F. P.

Simpson, D.—See Hawkings, R. C.

Simpson, S. D.—The synthesis of di- and trithiols, 20.

Singer, S. A. G.—See Breckenridge, J. G.

Sirianni, A. F., Wise, L. M., and McIntosh, R. L.—Osmotic pressure measurement and the instability of high polymers, 301.

Sivertz, C.—See Bardwell, J.

Southam, F. W. and Puddington, I. E.—The influence of the physical properties of sodium soaps on their dispersions in mineral oil, 121. The flow properties of some anhydrous sodium soaps, 125.

Spinks, J. W. T.—See Graham, W.

Stedman, D. F.—A periodic arrangement of the elements, 199.

Thode, H. G.—See Hawkings, R. C.; Lossing, F. P.; McGilvery, J.

Turcotte, F.—See L'Ecuyer, P.

Van Cleave, A. B. and Mitton, H. E.—The hydrolysis and polymerization of cyanogen chloride in the presence of hydrogen chloride, 430.

Wilkinson, G.—See Grummitt, W. E.

Winkler, C. A.—See Boyd, M. L.; Douglas, D. E.; Eastwood, T. A.; Hawkes, A. S.; Polley, J. R.

Wise, L. M.—See Sirianni, A. F.

Wright, G. F—See Allenby, O. C. W.; Bond, W. J.

Wright, R. H.—See Carroll, K. K.

Yaffe, L. and Mackintosh, C. E.—Fission yields of masses 131, 132, 134, and 136 formed in neutron fission of uranium, 371.
See Grummitt, W. E.

Young, E. G. and Campbell, R. B.—The reaction of β,β'-dichlorodiethyl sulphide with proteins, 37.

SECTION B

INDEX TO VOLUME 25

Subjects

Acetals and ketals, Cyclic,
  derived from 2,3-butanediol, Catalytic cracking of, 266.
  derived from *levo*-2,3-butanediol, 70.

Acetic acid
  esters, Cyano-, Synthesis of amino acids from, 4-Alkyl-3-aminopyrazolones, 28.
  Quantitative estimation of acetyl, ethylidene, ethoxy, and α-hydroxyethyl groups as, 485.
  – urotropine, Compound formation in the system,
    I. The phase diagram, 477.
    II. Raman spectrum measurements, 481.

Acetyl
  derivative of heparin, 472.
  group, Quantitative estimation of, as acetic acid, 485.

Acids, See Acetic; Aliphatic; Amino; Picric.

Activation, See Charcoal; Morden bentonite; Silica.

Adsorption
  of aliphatic acids on activated charcoals, 440.
  Preliminary observations of the dielectric constants of vapors adsorbed on activated silica, 566.

Air, Still and turbulent, Coagulation and surface losses in disperse systems in, 455.

Alcohol, See Ethyl alcohol.

Aliphatic acids, Adsorption of, on activated charcoals, 440.

Alkali, Hot, Effect of, on nitrates of starch, amylose, and amylopectin, 151.

4-Alkyl-3-aminopyrazolones, Synthesis of amino acids from cyanoacetic esters, 28.

Alloys, Zinc die-casting, Polarographic determination of tin in high purity zinc and, 322.

Aluminium silicates, Catalytic action of, I. The dehydration of butanediol-2,3 and butanone-2 over activated Morden bentonite, 80.

Amidopyrimidines, Sulphanil-, 14.

Amines, See Ethanolamine, Phenylenediamine.

Amino acids
  Synthesis of, from substituted cyanoacetic esters, 4-Alkyl-3-aminopyrazolones, 28.
  See Indole; Lysine.

Ammonium
  nitrate, Binary and ternary eutectics involving, 90.
  salts in aqueous solution, Studies on the formation of hexamine from formaldehyde and, 525.

Amylopectin, amylose, and starch, Effect of hot alkali on the nitrates of, 151.

Amylose, amylopectin, and starch, Effect of hot alkali on the nitrates of, 151.

Analysis, Method of, for the system: benzene – ethyl alcohol – carbon tetrachloride, 228.

Aromatization, Catalytic, of Turner Valley crudes, 108.

Azide, Lead, Thermal explosion of, 548.

***Bacillus subtilis*,** Fermentation of glucose by strains of, 56.

Bacteria,
  Fermentation of glucose by strains of *Bacillus subtilis*, 56.
  Dissimilation of glucose by *Serratia marcescens*, 65.

Barium
  Fission yields of Ba^{139} and Ba^{140} in neutron fission of U^{235} and U^{238}, 364.
  The growth of La^{140} (40 hours) from Ba^{140} (12.7 days), 357.

Bentonite, Activated Morden, Dehydration of butanediol-2,3 and butanone-2 over, 80.

Benzene
  – ethyl alcohol – carbon tetrachloride, A method of analysis for the system, 228.
  Evaluation of the intrinsic viscosity (as intrinsic flow time) of GR-S in, 333.
  Variation with temperature of the intrinsic viscosity of GR-S in, 351.
  See Dinitrobenzene.

Binary eutectics, See Eutectics.

1,3-Butadiene
1-Methoxy-, Preparation of, 118.
Reaction of cyanogen with, 272.
Theoretical aspects of the reaction of cyanogen and, 331.

2,3-Butanediol
Production and properties,
XVII. Fermentation of glucose by strains of *Bacillus subtilis*, 56.
XVIII. Dissimilation of glucose by *Serratia marcescens*, 65.
XIX. Cyclic acetals and ketals derived from *levo*-2,3-butanediol, 70.
XXI. Catalytic cracking of cyclic acetals and ketals derived from 2,3-butanediol, 266.
XXIII. Condensation of the isomeric 2,3-butanediols with ethyl acetoacetate, 423.
XXIV. The cyclic sulphites of *meso*- and *levo*-2,3-butanediol, 491.
and butanone-2, Dehydration of, over activated Morden bentonite, 80.

Butanone-2 and butanediol-2,3, Dehydration of, over activated Morden bentonite, 80.

Calcium, Photometric microdetermination of, 449.

Carbazole derivatives, Synthesis of some, 376.

Carbohydrates and polysaccharides,
Studies on reactions relating to,
*LXII. Effect of hot alkali on the nitrates of starch, amylose, and amylopectin, 151.
*LXIII. The stability of maltose and cellobiose octanitrates, 155.

Carbon, Isotopes of, Recording of, with a recording unit and electronic shunt selector for a mass spectrometer, 397.

Carbon tetrachloride – ethyl alcohol – benzene, A method of analysis for the system, 228.

Catalytic action of aluminium silicates, I. The dehydration of butanediol-2,3 and butanone-2 over activated Morden bentonite, 80.

Catalytic aromatization of Turner Valley crudes, 108.

Catalytic cracking of cyclic acetals and ketals derived from 2,3-butanediol, 266.

Catalytic oxidation of pure methane at high pressures using copper, silver, zinc, nickel, or Monel metal as catalysts, 494.

Cellobiose and maltose, Stability of octanitrates of, 155.

Characterization and synthesis of monomethyl- and dimethylindoles, 1.

Charcoal, Activated
Adsorption of aliphatic acids on, 440.
Cocoanut-shell, Heterogeneity of, 502.

Chromates of silver and copper, 243.

Coagulation and surface losses in disperse systems in still and turbulent air, 455.

Cocoanut-shell charcoal, Activated, Heterogeneity of, 502.

Colorimetry
Rapid method for the determination of lysine in protein hydrolysates, 540.
Photometric microdetermination of calcium, 449.
Reagent for ruthenium, 5-Hydroxyquinoline-8-carboxylic acid, 49.

Compound formation in the system urotropine – acetic acid,
I. The phase diagram, 477.
II. Raman spectrum measurements, 481.

Consecutive second order reactions, Kinetics of, 415.

Copper
As catalyst in the oxidation of methane at high pressures, 494.
chromates, 243.

Cracking, Catalytic, of cyclic acetals and ketals derived from 2,3-butanediol, 266.

Crystallization
characteristics and equilibrium data of the system: picric acid – dinitrophenol – picramide, 211.
velocities and equilibrium diagrams of the systems: (a) picric acid – 2,4-dinitrophenol, (b) dinitrophenol – trinitrotoluene, (c) picric acid – dinitrophenol – trinitrotoluene, 183.

Cure, Measurements of, of some thermosetting resins, 101.

Cyanoacetic esters, Synthesis of amino acids from, 4-Alkyl-3-aminopyrazolones, 28.

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* *See Errata at the end of this Index.*

Cyanogen
chloride
Hydrolysis and polymerization of, in the presence of hydrogen chloride, 430.
Preparation of, 289.
Preparation, purification, physical properties, and hydrolysis of, 381.
Concerning the theoretical aspects of the reaction of 1,3-butadiene with, 331.
Preparation of 2-cyanopyridines from some simple dienes and, 283.
Reaction of 1,3-butadiene with, 272.

2-Cyanopyridines, Preparation of, from cyanogen and some simple 1,3-dienes, 283.

Cyclic acetals and ketals
derived from 2,3-butanediol, Catalytic cracking of, 266.
derived from *levo*-2,3-butanediol, 70.

Cyclic sulphites of *meso-* and *levo*-2,3-butanediol, 491.

Decomposition, Thermal, of hydrogen peroxide vapor, II, 135.

DDT, Studies in the formation of, 509.

Dehydration of butanediol-2,3 and butanone-2 over activated Morden bentonite, 80.

β,β′-Dichlorodiethyl sulphide, Reaction of, with proteins, 37.

Dielectric constants of vapors adsorbed on activated silica, Preliminary observations of, 566.

1,3-Dienes
Preparation of 2-cyanopyridines from cyanogen and some simple 1,3-dienes, 283.
See Butadiene.

Dimethyldinitroöxamide, 295.

Dinitrobenzene, trinitrotoluene, RDX, and NENO, A study of systems involving, with particular reference to the composition of the binary eutectics, 216.

Dinitrodimethyloxamide, 295.

2,4-Dinitrophenol
– picric acid, Equilibrium diagrams and crystallization velocities of the system, 183.
– picric acid – picramide, Equilibrium data and crystallization characteristics of the system, 211.
– picric acid – trinitrotoluene, Equilibrium diagrams and crystallization velocities of the system, 183.
– trinitrotoluene, Equilibrium diagrams and crystallization velocities of the system, 183.

Disperse systems, Coagulation and surface losses in, in still and turbulent air, 455.

Dispersions in mineral oil, Influence of the physical properties of sodium soaps on their, 121.

Dissimilation of glucose by *Serratia marcescens*, 65.

Distyryl and stilbene, Meerwein reaction applied to the synthesis of derivatives of, 575.

Dithiols and trithiols, Synthesis of, 20.

Electrodes, Multi-tip, Note on the use of, in polarographic work, 132.

Electronic shunt selector and recording unit for a mass spectrometer, 397.

Elements, Periodic arrangement of, 199.

Equilibrium
data and crystallization characteristics of the system: picric acid – dinitrophenol – picramide, 211.
diagrams and crystallization velocities of the systems: (a) picric acid – 2,4-dinitrophenol; (b) dinitrophenol – trinitrotoluene; (c) picric acid – dinitrophenol – trinitrotoluene, 183

Ethanolamines, Kinetics of formation, 405.

Ethoxy group, Quantitative estimation of, as acetic acid, 485.

Ethyl acetoacetate, Condensation of the isomeric 2,3-butanediols with, 423.

Ethyl alcohol – benzene – carbon tetrachloride, A method of analysis for the system, 228.

Ethyl, α-Hydroxy-, group, Quantitative estimation of, as acetic acid, 485.

Ethylidene group, Quantitative estimation of, as acetic acid, 485.

Eutectics
Binary, A study of systems involving trinitrotrotoluene, RDX, NENO, and dinitrobenzene, with particular reference to the composition of, 216.
Binary and ternary, Involving ammonium nitrate, 90.

Explosion, Thermal, of lead azide, 548.

Fermentation of glucose by strains of *Bacillus subtilis*, 56.

Fission yields
  of Ba ^{139} and Ba^{140} in neutron fission of U^{235} and U^{238}, 364.
  of masses 131, 132, 134, and 136 formed in neutron fission of uranium, 371.

Flow
  properties of some anhydrous sodium soaps, 125.
  time, Intrinsic, Evaluation of the intrinsic viscosity of GR-S in benzene as, 333.

Formaldehyde, Studies on the formation of hexamine from ammonium salts and, in aqueous solution, 525.

Fractionation of the reaction product of linseed oil and glycerol, 420.

Glucose
  Dissimilation of, by *Serratia marcescens*, 65.
  Fermentation of, by strains of *Bacillus subtilis*, 56.

Glycerol and linseed oil, Fractionation of the reaction product of, 420.

Growth of La^{140} (40 hours) from Ba^{140} (12.7 days), 357.

GR-S
  Intrinsic viscosity in benzene
    Evaluation of (as intrinsic flow time), 333.
    Variation of, with temperature, 351.
  polymerizations, Tertiary mercaptans as modifiers in, 159.

Heparin, Acetyl derivative of, 472.

Heterogeneity of activated cocoanut-shell charcoal, 502.

Hexamine
  Formation of, Studies on, 387.
  from formaldehyde and ammonium salts in aqueous solution, Studies on the formation of, 525.

Hydrogen chloride, Hydrolysis and polymerization of cyanogen chloride in the presence of, 430.

Hydrogen peroxide, Thermal decomposition of the vapor of, II, 135.

Hydrolysis
  of cyanogen chloride, 381.
  and polymerization of cyanogen chloride in the presence of hydrogen chloride, 430.

α-Hydroxyethyl group, Quantitative estimation of, as acetic acid, 485.

5-Hydroxyquinoline-8-carboxylic acid, A colorimetric reagent for ruthenium, 49.

Indoles, Monomethyl- and dimethyl-, Synthesis and characterization of, 1.

Instability and osmotic pressure measurement of high polymers, 301.

Intrinsic viscosity of GR-S in benzene
  Evaluation of (as intrinsic flow time), 333.
  Variation of, with temperature, 351.

Isomeric 2,3-butanediols, Condensation of, with ethyl acetoacetate, 423.

Isotopes, See Barium; Carbon; Lanthanum; Neutron fission; Uranium; Xenon.

Ketals and acetals, Cyclic,
  Catalytic cracking of, derived from 2,3-butanediol, 266.
  derived from *levo*-2,3-butanediol, 70.

Kinetics
  of consecutive second order reactions, 415.
  of the formation of ethanolamines, 405.

Lanthanum, The growth of La^{140} (40 hours) from Ba^{140} (12.7 days), 357.

Lead azide, Thermal explosion of, 548.

Light scattering, Determination of particle size by means of, 255.

Lignin, Sassafras, Isolation of, 535.

Linseed oil and glycerol, Fractionation of the reaction product of, 420.

Lysine in protein hydrolysates, Rapid colorimetric method for the determination of, 540.

Maltose and cellobiose, Stability of octanitrates of, 155.

Mass spectrometer, Recording unit and electronic shunt selector for, 397.

Masses 131, 132, 134, and 136 formed in neutron fission of uranium, Fission yields of, 371.

Meerwein reaction applied to the synthesis of distyryl and stilbene derivatives, 575.

Mercaptans, Tertiary, As modifiers in GR-S polymerizations, 159.

Methane, Oxidation of, at high pressures, IV. Experiments using pure methane and copper, silver, zinc, nickel, or Monel metal as catalysts, 494.

1-Methoxy-1,3-butadiene, Note on the preparation of, 118.

Microdetermination of calcium, Photometric, 449.

Mineral oil, Influence of the physical properties of sodium soaps on their dispersions in, 121.

Modifiers in GR-S polymerizations, Tertiary mercaptans as, 159.

Monel metal, As catalyst in the oxidation of methane at high pressures, 494.

Morden bentonite, Activated, Dehydration of butanediol-2,3 and butanone-2 over, 80.

Mustard gas, Reaction of β,β'-dichlorodiethyl sulphide with proteins, 37.

NENO, trinitrotoluene, RDX, and dinitrobenzene, A study of systems involving, with particular reference to the composition of the binary eutectics, 216.

Neutron fission
  of uranium, Fission yields of masses 131, 132, 134, and 136 formed in, 371.
  of U^{235} and U^{238}, Fission yields of Ba ^{139} and Ba^{140} in, 364.

Nickel, As catalyst in the oxidation of methane at high pressures, 494.

Nitrate(s)
  Ammonium, See Ammonium nitrate.
  Octa-, of maltose and cellobiose, Stability of, 155.
  of starch, amylose, and amylopectin, Effect of hot alkali on, 151.

Octanitrates of maltose and cellobiose, Stability of, 155.

Oil
  Linseed, See Linseed oil.
  Mineral, Influence of the physical properties of sodium soaps on their dispersions in, 121.
  Turner Valley crudes, Catalytic aromatization of, 108.

Osmotic pressure measurement and the instability of high polymers, 301.

Oxamide, Dimethyldinitro-, 295.

Oxidation of methane at high pressures. IV. Experiments using pure methane and copper, silver, zinc, nickel, or Monel metal as catalysts, 494.

Particle size, Determination of, by light scattering, 255.

Periodic arrangement of the elements, 199.

Peroxide, Hydrogen, Thermal decomposition of vapor of, II, 135.

Phase diagram of the system urotropine – acetic acid showing compound formation, 477.

1,10-Phenanthroline, Preparation of, from *o*-phenylenediamine, 583.

Phenol, See Dinitrophenol.

***o*-Phenylenediamine,** Preparation of 1,10-phenanthroline from, 583.

Photometric microdetermination of calcium, 449.

Physical properties
  of cyanogen chloride, 381.
  of sodium soaps, Influence of, on their dispersions in mineral oil, 121.

Picramide – picric acid – dinitrophenol, Equilibrium data and crystallization characteristics of the system, 211.

Picric acid
– 2,4-dinitrophenol, Equilibrium diagrams and crystallization velocities of the system, 183.
  – dinitrophenol – picramide, Equilibrium data and crystallization characteristics of the system, 211.
  – dinitrophenol – trinitrotoluene, Equilibrium diagrams and crystallization velocities of the system, 183.

Piperonyl nucleus, Presence of, in sassafras lignin, 535.

Polarographic determination of tin in high purity zinc and zinc die-casting alloys, 322.

Polarography, Note on the use of multi-tip electrodes in, 132.

Polymerization
  and hydrolysis of cyanogen chloride in the presence of hydrogen chloride, 430.
  GR-S, Tertiary mercaptans as modifiers in, 159.

Polymers
  High, Osmotic pressure measurement and instability of, 301.
  See Resins.

Polysaccharides and carbohydrates, See Carbohydrates and polysaccharides.

Pressure(s)
  High, Oxidation of pure methane at, using copper, silver, zinc, nickel, or Monel metal as catalysts, 494.
  Osmotic, See Osmotic pressure.

Protein
  hydrolysates, Rapid colorimetric method for the determination of lysine in, 540.
  Reaction of β,β'-dichlorodiethyl sulphide with, 37.

Purification of cyanogen chloride, 381.

Pyrazolones, 4-Alkyl-3-amino, Synthesis of amino acids from substituted cyanoacetic esters, 28.

Pyridines, 2-Cyano-, Preparation of, from cyanogen and some simple 1,3-dienes, 283.

Pyrimidine, Sulphanilamido-, 14.

Quinoline-8-carboxylic acid, 5-Hydroxy-, A colorimetric reagent for ruthenium, 49.

Raman spectrum measurements, Compound formation in the system urotropine – acetic acid, 481.

RDX, trinitrotoluene, NENO, and dinitrobenzene, A study of systems involving, with particular reference to the composition of the binary eutectics, 216.

Reactions(s)
  Meerwein's, Application of, to the synthesis of stilbene and distyryl derivatives, 575.
  of cyanogen with 1,3-butadiene, 272.
  of cyanogen and 1,3-butadiene, Concerning the theoretical aspects of, 331.
  of β,β'-dichlorodiethyl sulphide with proteins, 37.
  product of linseed oil and glycerol, Fractionation of, 420.
  Second order, Kinetics of, 415.
  See Carbohydrates and polysaccharides.

Reaction kinetics, See Kinetics.

Recording unit and electronic shunt selector for a mass spectrometer, 397.

Resins, Thermosetting, Measurements of cure of some, 101.

Rubber, Synthetic, See GR-S.

Ruthenium, Colorimetric reagent for, 5-Hydroxyquinoline-8-carboxylic acid, 49.

Sassafras lignin, Isolation of, 535.

Scattering of light, Determination of particle size by means of, 255.

Second order reactions, Consecutive, Kinetics of, 415.

Serratia marcescens, Dissimilation of glucose by, 65.

Shunt selector, Electronic, and recording unit for a mass spectrometer, 397.

Silica, Activated, Preliminary observations of the dielectric constants of vapors adsorbed on, 566.

Silicates, Aluminium, Catalytic action of, I. The dehydration of butanediol-2,3 and butanone-2 over activated Morden bentonite, 80.

Silver
  As a catalyst in the oxidation of methane at high pressures, 494.
  chromates, 243.

Soaps, Sodium, See Sodium soaps.

Sodium soaps
  Anhydrous, Flow properties of some, 125.
  Physical properties of, Influence of, on their dispersions in mineral oil, 121.

Spectrum, Raman, See Raman spectrum.

Stability of maltose and cellobiose octanitrates, 155.

Starch, amylose, and amylopectin, Nitrates of, Effect of hot alkali on, 151.

Stilbene and distyryl, Meerwein reaction applied to the synthesis of derivatives of, 575.

Sulphanilamidopyrimidines, 14.

Sulphide, β,β'-Dichlorodiethyl-, Reaction of, with proteins, 37.

Sulphites, Cyclic, of *meso-* and *levo*-2,3-butanediol, 491.

Surface losses and coagulation in disperse systems in still and turbulent air, 455.

Synthesis
  of amino acids, from substituted cyanoacetic esters, 4-Alkyl-3-aminopyrazolones, 28.
  of carbazole derivatives, 376.
  of cyanogen chloride, 289, 381.
  of 2-cyanopyridines from cyanogen and some simple 1,3-dienes, 283.

Synthesis—(*cont.*)
  of derivatives of stilbene and distyryl, Meerwein reaction applied to, 575.
  of di- and trithiols, 20.
  of 1-methoxy-1,3-butadiene, Note on, 118.
  of monomethyl- and dimethylindoles, 1.
  of 1,10-phenanthroline from *o*-phenylenediamine, 583.
  See Butanediol; DDT; Hexamine.

System(s)
  Benzene - ethyl alcohol - carbon tetrachloride, Method of analysis for, 228.
  Disperse, Coagulation and surface losses in, in still and turbulent air, 455.
  involving trinitrotoluene, RDX, NENO, and dinitrobenzene, Study of, with particular reference to the composition of the binary eutectics, 216.
  (*a*) picric acid - 2,4-dinitrophenol; (*b*) dinitrophenol - trinitrotoluene; (*c*) picric acid - dinitrophenol - trinitrotoluene; Equilibrium diagrams and crystallization velocities of, 183.
  picric acid - dinitrophenol - picramide, Equilibrium data and crystallization characteristics of, 211.
  urotropine - acetic acid, Compound formation in,
    I. The phase diagram, 477.
    II. Raman spectrum measurements, 481.

Temperature, Variation with, of the intrinsic viscosity of GR-S in benzene, 351.

Ternary eutectics, See Eutectics.

Tertiary mercaptans as modifiers in GR-S polymerizations, 159.

Thermal decomposition of hydrogen peroxide vapor, II, 135.

Thermal explosion of lead azide, 548.

Thermosetting resins, Measurements of cure of some, 101.

Thiols, Di- and tri-, Synthesis of, 20.

Tin, Polarographic determination of, in high purity zinc and zinc die-casting alloys, 322.

Toluene, See Trinitrotoluene.

Trinitrotoluene
  - dinitrophenol, Equilibrium diagrams and crystallization velocities of the system, 183.
  - picric acid - dinitrophenol, Equilibrium diagrams and crystallization velocities of the system, 183.
  RDX, NENO, and dinitrobenzene, A study of systems involving, with particular reference to the composition of the binary eutectics, 216.

Trithiols and dithiols, Synthesis of, 20.

Turner Valley crudes, Catalytic aromatization of, 108.

Uranium
  Neutron fission of, Fission yields of masses 131, 132, 134, and 136 formed in, 371.
  fission yields of Ba^{139} and Ba^{140} in neutron fission of U^{235} and U^{238}, 364.

Urotropine - acetic acid, Compound formation in the system,
  I. The phase diagram, 477.
  II. Raman spectrum measurements, 481.

Vapor(s)
  adsorbed on activated silica, Preliminary observations of the dielectric constants of, 566.
  Hydrogen peroxide, Thermal decomposition of, 135.

Viscosity, Intrinsic, of GR-S in benzene, Evaluation of (as intrinsic flow time), 333. Variation of, with temperature, 351.

Xenon, Isotopes of, Recording of, with a recording unit and electronic shunt selector for a mass spectrometer, 397.

Zinc
  as catalyst in the oxidation of methane at high pressures, 494.
  Polarographic determination of tin in high purity zinc and zinc die-casting alloys, 322.

ERRATA

Four papers appearing recently in the Canadian Journal of Research were incorrectly numbered in the series "Studies on Reactions Relating to Carbohydrates and Polysaccharides". The correct numbering of these papers is shown below:—

Section B, Vol. 24, 1946, page 238, for "LX" read "LXVIII".
Section B, Vol. 24, 1946, page 246, for "LXI" read "LXIX".
Section B, Vol. 25, 1947, page 151, for "LXII" read "LXX".
Section B, Vol. 25, 1947, page 155, for "LXIII" read "LXXI".

Page 543, end of Section (9), add: "The reagent is finally diluted 3 to 10".

Page 544, under "Chlorination and Colorimetry", lines 5 and 6, for "sufficient to adjust the solution" read "so that the final solution containing the phenol reagent is adjusted".

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